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Scavenging of Pollutants by Marine Aerosols

Atmospheric Research Group, Altadena, Calif

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National Environmental Research Center, Research Triangle Park, N C
Meteorology Lab

9 Aug 74

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SCAVENGING OF POLLUTANTS BY MARINE AEROSOLS

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Final Report

SCAVENGING OF POLLUTANTS BY MARINE AEROSOLS

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To

Environmental Protection Agency
National Environmental Research Center
Division of Meteorology
Research Triangle Park, North Carolina 27711

From

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9 August 1974

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I. INTRODUCTION

In recent years the physical and chemical concepts of the marine aerosol have changed significantly. Until recent measurements were made, this aerosol was believed to be the simple residue of evaporated sea spray. Each particle was believed to have a chemical composition identical to the ratio of dissolved salts in the oceans. Today this concept has changed and evidence exists that the marine aerosol may be as complex as the particulate composition of the atmosphere over the continents.

Organic films aerosolized by bubbles bursting at the ocean's surface (Garrett, 1964; Garrett, 1968) are carried into the marine atmosphere and have been identified as a component of the aerosol. Some organic material is associated with all salt particles (Goetz, 1965; Blanchard, 1968) while other evidence exists to imply that much of the bubble forming organics appear in the finer aerosol fraction (Pueschel, et. al., 1969).

Extensive mixing of continental air in the marine environment has been observed along coastal regions (Holzworth, 1959; Green, 1972, and others). The effect of this mixing adds large quantities of small (less than 1 μm) particles derived from combustion and other terrestrial sources.

Interactions between gases and marine aerosols are supported by theoretical, experimental (Robbins, et. al., 1959) and observational (Junge, 1956; Green, 1972) evidence. Anomalies with respect to sea water have been observed frequently in the ratios of halogen ions in marine aerosols (Duce, et. al., 1965; Duce, et. al., 1966).

All these earlier observations have been supported and expanded upon by recent work at various laboratories and field sites throughout the world.

The approach in this study was twofold. By using the Los Angeles basin as an acknowledged source of oxidants, fine pollution particulates and oxides of nitrogen, it was possible to study certain extremes in the interaction between these elements of the continental air mass and the local coastal marine environment. Secondly, by selecting the proper meteorological conditions for persistent onshore wind flow, it was potentially possible to observe a nearly pure marine aerosol which could be used as a reference or baseline for other measurements along the southern California coast.

II. LOCATION - LOS ANGELES BASIN

The Los Angeles basin and adjoining coastline provide an excellent site to study interactions between marine and continental air. The dominant air flow pattern at ground level is characterized by diurnal oscillations of the marine layer. At night, offshore winds carry polluted air several miles out over the ocean, allowing aerosols generated at the ocean surface to mix into a richly charged atmosphere of fine combustion particles and oxidizing gases.

As soon as the air flow is reversed and moves onshore during the day, this modified, but still contaminated, air can be studied easily from coastal sampling stations. Later in the day, after the passage of the seaward "smog front", relatively clean maritime air is swept across the coastline until the flow is reversed again that night.

Occasionally, this dominant diurnal pattern is interrupted by either strong offshore "Santa Ana" winds or a strong reverse onshore flow controlled by a sharp gradient between a coastal basin and a deep low pressure system over the Colorado plateau.

Some aspects of the interactions between polluted continental air and the marine environment are discussed in Attachment A (Green, 1972). The body of this report will deal with further data on this interaction, particularly with respect to the influence of the basin and its high output of nitrogen oxides on the chemical composition of the maritime aerosol.

III. METEOROLOGICAL AND SAMPLING CONDITIONS

As mentioned before, the air flow patterns on the coast of southern California can be characterized as diurnal oscillation, offshore "Santa Ana", or persistent onshore. For the purposes of this study, the "Santa Ana" condition was excluded. The diurnal pattern had been studied before in Attachment A, however, additional data was collected. One previous omission had been a continuous documentation of the complete cycle. Toward this end, a full cycle of aerosol and meteorological data was collected between 10 October 1972 and 12 October 1972.

The principal goal of this study was to examine the nature of maritime air derived under the persistent onshore wind condition. Generally, sampling dates were selected where little or no offshore reversal had occurred for three to five days. By sampling this type of air, it was hoped that relatively pure and uncontaminated marine aerosols could be sampled. With one exception, this did not prove to be the case.

The shoreline sampling site was identical to the one used for the work referenced in Attachment A. Samples were collected at the 46-meter and 12-meter levels rather than at 30 meters and 8 meters.

An inland site was selected at Hawthorne about 5 Km from El Segundo to collect correlative data. Samples collected at this station, augmented by meteorological support data, provided measurements of mixed surf and maritime aerosol moving onshore as well as the incorporation of dust and other continental aerosols picked up in transit.

At El Segundo, the 46-meter level provided the opportunity to sample aerosols arriving from the open ocean before a surf spray component had been added from breakers on the beach. The 12-meter level, by contrast, was dominated by material from the surf line. A sharp distinction in the chemical and physical properties of aerosols at the two levels was almost always present.

The location of the El Segundo and Hawthorne sites are shown on the outline map of the Los Angeles coastal basin in Figure 1. A schematic of the two stations in exaggerated relief is presented in Figure 2.

Fig. 1. COASTAL AEROSOL TRANSPORT AND INTERACTION STUDIES
LOS ANGELES, CALIFORNIA

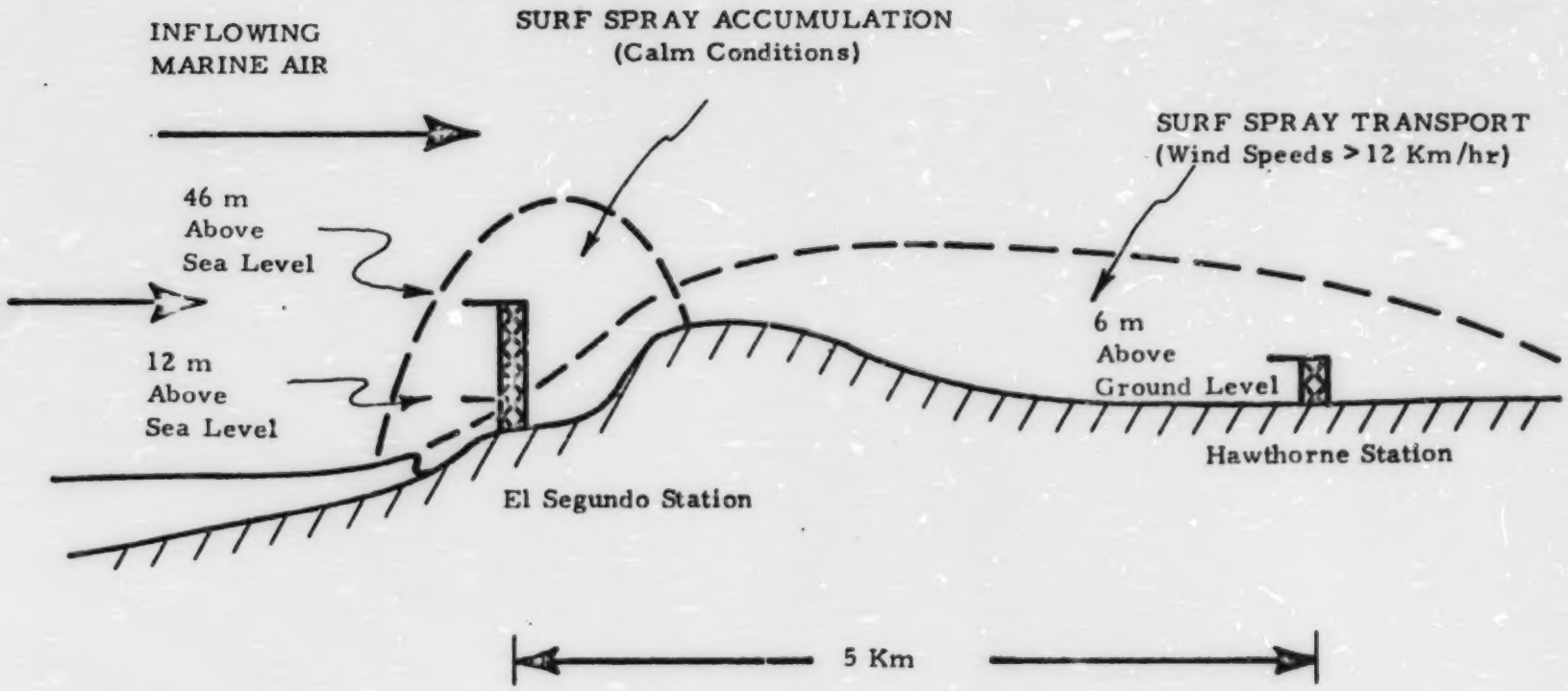

Fig. 2. SAMPLING STATIONS AND PARTICLE DISTRIBUTION AT EL SEGUNDO - HAWTHORNE RANGE

Generally, the coastal samples were taken at the 46-meter level to avoid the surf component. The lower 12-meter level was used only once in conjunction with the 46-meter level, during the extended sampling period on 10-12 October 1972. At that time, particularly under calm wind conditions, it was possible to get an index of the direct vertical mixing rate.

IV. MEASUREMENTS AND TREATMENT OF DATA

Preweighed 8" x 10" glass fiber filters were used with a high volume air sampler to collect aerosol samples. Once the filters were reweighed, the total aerosol concentration (in $\mu g/m^3$) during the sampling period was calculated from the change in mass, average flow rate and length of sampling time. In general, aerosol samples were taken between 1-1/2 and 3 hours each with average flow rates of approximately 60-80 cfm.

The soluble solids collected on the filters were then extracted and analyzed for chloride ion and nitrate ion. In addition, unused filters were analyzed to establish the blank values of the above constituents.

The relative humidity data for El Segundo and Hawthorne were calculated from wet bulb-dry bulb readings taken with a sling psychrometer.

At El Segundo, wind speed and wind direction data were obtained from permanently installed meteorological instrumentation, while at Hawthorne, these data were obtained from an MRI mechanical weather station located on the sampling platform.

These data were used to calculate the source-production-ventilation parameter, $\overline{SD}/V_L$, discussed in the next section.

The hourly average data of the gaseous pollutants, NO_2 and NO, were obtained from the Los Angeles Air Pollution Control District office located in Lennox, California, approximately 5 Km north of Hawthorne and about 6 Km from the coast. From these data, and from water vapor concentrations determined from temperature and relative humidity, equilibrium concentrations of nitric acid vapor were calculated using the equation

$$\left[HNO_{3_{vap.}}\right] = \left(\frac{0.004\ (NO_2)^3\ (H_2O)}{(NO)}\right)^{1/2} \qquad (1)$$

Values of (HNO_3 e.q.) for the Hawthorne samples are shown in the following section. Their significance and the origin of equation (1) will be discussed in a later section.

V. RESULTS

A total of 38 separate filter samples were collected at the 46-meter level at El Segundo between 19 April 1972 and 12 October 1972. Each filter was weighed to determine total aerosol collected. Average aerosol concentration in the air sampled was calculated from the average flow rate. After weighing, each filter was analyzed for chloride and nitrate ions.

Nitrate ion represents a very small and almost negligible percentage of the dissolved salt in the ocean. It was assumed, therefore, that the measured nitrate was derived principally from reactions between nitrogen dioxide, water and chloride ion. The nitric acid was being converted to sodium nitrate and chloride was being lost as hydrochloric acid or gaseous chlorine (Green, 1972).

These reactions are

$$3NO_2 + H_2O_{vapor} \rightleftarrows 2HNO_3 + NO \qquad (2)$$

or

$$2NO_2 + H_2O_{liquid} \rightleftarrows HNO_2 + HNO_3 \qquad (3)$$

with the latter being favored on an equilibrium basis.

Nitric acid then reacts with chloride in the aerosol according to the equation

$$HNO_3 + NaCl \rightleftarrows Na\,NO_3 + HCl \qquad (4)$$

The chloride and nitrate analyses were used in this study to calculate the equivalent sea salt concentrations in the aerosol samples. When NO_3 reacts, as in Eq. (4), it was assumed that for each mole of nitrate formed, a mole of chloride was lost as hydrogen chloride. By weight, each measured unit of nitrate was equivalent to 0.57 units of chloride. Using these relationships, the measured nitrate was converted back to equivalent chloride ion. The sum of the actual chloride ion plus chloride ion inferred from the nitrate conversion was used to calculate the total equivalent sea salt assuming the aerosols contained the sea salt value of 55 percent by weight chloride.

In Table I, the aerosol and source data are summarized for the 46-meter level at El Segundo. C is the total aerosol concentration in $\mu g/m^3$. C'' is the equivalent sea salt as calculated from the chloride and nitrate values. C''/C is an index of the ratio of sea salt and other aerosol materials in the sample. With the exception of one date (25 May 1972) which is in question and another date (9 June 1972), none of the samples approached a pure marine aerosol.

The source-production-ventilation parameter, $\bar{S}D/V_L$, in the last column of Table I proved to be the best means of correlating the measured types of aerosols with the conditions leading to the formation of the aerosol.

The source distance, D in miles, was the total over water wind run prior to sampling. The duration of this flow was determined from the last incidence of mild offshore winds. As will be discussed later, this term proved to be more valuable in defining local wind flow. Some of the larger distances in Table I proved to represent large scale circulation of offshore air from the Pacific Northwest and not air that originated far offshore in the Pacific Ocean.

$\bar{S}$ is an average sea state calculated from a combination of local observations and the average wind speed. It represents a salt spray or surface agitation term leading to the production of salt aerosols. A combination of $\bar{S}$ and D was used as the inferred salt production term.

V_L is the local wind speed at the time of sampling and has been used as an inverse measure of the vertical mixing or turbulence which would dilute the salt rich air near the air-sea boundary layer with air from above.

The data in Table II for the 12-meter level at El Segundo was taken only during the 24-hour sampling period on 11 and 12 October 1972. Chemical analyses were performed on only three of the eight filters collected.

Table III contains the data collected at Hawthorne. These samples were taken generally in the same time periods as the samples in Tables I and II. As a result, it was possible to make correlations of changes in the aerosol as it was transported inland from El Segundo 5 Km to Hawthorne. Generally, all these

Table I

DATA SUMMARY
EL SEGUNDO 46-METER ASL

Date	Sampling Period	Filter Number	Composition Concentration ($\mu g/m^3$)			Production Rate Average Sea State $\bar{S}$	Source (Miles Offshore) D	Wind Speed V_L	Aerosol Production Ventilation Parameter $\bar{S}D/V_L$
			C Total Aerosol	C' Equiv. Sea Salt($Cl^- - NO_3^-$)	C''/C				
4-19-72	1513-1621	285	54.8	27.7	0.51	1.89	11.4	3.0	7.18
	1625-1800	284	36.7	21.0	0.57	1.89	16.1	2.3	13.23
4-25-72	1040-1212	283	49.6	30.4	0.61	2.40	16.8	8.6	4.60
5-4-72	1200-1325	279	38.0	17.8	0.47	2.00	481.9	6.8	141.74
	1330-1455	282	28.8	12.9	0.45	2.01	491.1	8.5	116.13
	1500-1635	281	28.7	11.4	0.40	2.02	505.6	7.2	141.85
5-5-72	1745-1950	289	38.6	8.6	0.22	2.05	635.0	8.2	158.75
5-10-72	1500-1650	287	65.3	17.7	0.27	2.40	52.7	9.9	12.78
5-17-72	1305-1425	355	71.8	12.7	0.18	2.05	175.7	9.7	37.13
	1439-1519	329	58.9	13.9	0.24	2.06	185.6	9.9	38.62
	1524-1631	330	48.5	14.0	0.29	2.07	194.8	9.7	41.57
	1635-1745	331	45.2	12.2	0.27	2.09	204.0	9.2	46.34
5-24-72	1500-1630	353	38.9	17.5	0.45	1.89	46.2	5.9	14.80
5-25-72	1435-1530	407	18.5	27.8	[1.50]	1.93	166.2	8.9	36.04
6-5-72	1525-1645	350	73.9	21.4	0.29	2.02	61.0	9.2	13.39
6-9-72	1140-1250	401	36.5	22.4	0.61	1.96	370.0	6.1	118.89
	1305-1423	402	13.3	14.4	[1.08]	1.97	388.5	9.2	83.19
	1431-1530	403	8.2	9.4	[1.15]	1.98	401.5	12.1	65.70
	1537-1643	404	8.9	9.7	[1.09]	1.99	419.3	11.2	74.50
6-15-72	1630-1715	244	12.0	6.5	0.54	2.13	211.1	8.3	54.17
6-22-72	1334-1535	426	28.8	4.3	0.21	1.95	193.9	5.4	70.02
6-28-72	0948-1030	396	114.7	19.5	0.17	2.06	423.7	6.9	126.50
	1500-1630	424	43.7	9.5	0.22	2.09	479.2	9.6	104.33
	1635-1750	425	73.7	9.6	0.13	2.09	487.1	8.3	122.66
6-29-72	1415-1515	257	66.4	12.7	0.19	1.89	60.6	7.7	14.87
8-30-72	0839-1014	255	161.2	41.2	0.26	1.89	-33.6	6.8	-9.34
	1019-1245	247	119.2	40.6	0.34	1.89	-54.0	6.9	-14.79
	1313-1530	267	43.9	22.2	0.51	1.89	-63.3	4.8	-24.92
9-6-72	1321-1501	260	61.8	23.6	0.38	2.29	81.8	10.4	18.01
	1509-1700	261	44.7	23.6	0.53	2.26	86.4	8.9	21.94
10-11-72	0908-1208	605	60.89	21.49	0.35	1.89	12.0	3.0	7.56
	1216-1514	606	53.58			1.89	36.0	7.5	9.07
	1519-1819	607	21.73			2.23	76.0	12.5	13.56
	1825-2118	608	13.87	4.39	0.32	1.89	108.0	11.0	18.56
	2125-2413	609	26.68			1.89	131.0	8.0	30.95
10-12-72	2417-0308	610	67.48			1.89	141.0	5.0	53.30
	0320-0710	616	61.70	16.07	0.26	1.89	149.0	4.0	70.40
	0715-1015	611	126.59			1.89	5.0	3.8	3.38

Table II

DATA SUMMARY
EL SEGUNDO 12- METER ASL

Date	Sampling Period	Filter Number	Composition Concentration ($\mu g/m^3$)			Production Rate Average Sea State $\overline{S}$	Source (Miles Offshore) D	Wind Speed V_L	Aerosol Production Ventilation Parameter $\overline{SD}/V_L$
			C Total Aerosol	C" Equiv. Sea Salt(Cl^--NO_3^-)	C"/C				
10-11-72	0900-1156	593	219.56	92.29	0.42	1.89	12.0	3.0	7.56
	1203-1457	594	170.26			1.89	36.0	7.5	9.07
	1502-1802	595	104.39			2.23	76.0	12.5	13.56
	1808-2055	596	89.20	45.83	0.51	1.89	108.0	11.0	18.56
	2108-2355	597	158.19			1.89	131.0	8.0	30.95
10-12-72	2400-0300	598	176.68			1.89	141.0	5.0	53.30
	0305-0640	599	111.33	38.09	0.34	1.89	149.0	4.0	70.40
	0650-0950	600	120.59			1.89	5.0	2.8	3.38

Table III

DATA SUMMARY
HAWTHORNE 6-METER AGL

Date	Sampling Period	Filter Number	Composition Concentration ($\mu g/m^3$)			Production Rate Average Sea State $\bar{S}$	Source (Miles Offshore) D	Wind Speed V_L	Aerosol Production Ventilation Parameter $\bar{S}D/V_L$
			C Total Aerosol	C'' Equiv. Sea Salt($Cl^- - NO_3^-$)	C''/C				
4-19-72	1350-1622	291	33.9	13.6	0.40	1.89	14.2	3.0	8.95
	1628-1738	290	28.9	16.7	0.58	1.89	19.9	2.3	16.35
4-25-72	1215-1320	280	86.9	32.0	0.37	2.40	22.6	8.6	6.31
5-4-72	1030-1229	324	41.2	8.9	0.22	1.99	473.9	5.0	188.61
	1241-1414	321	44.7	3.1	0.07	2.00	483.6	6.8	142.24
	1420-1550	276	36.9	10.4	0.28	2.01	499.6	8.8	114.11
	1558-1735	277	35.2	7.4	0.21	2.03	516.6	7.0	149.81
5-5-72	1825-1915	286	32.2	13.4	0.42	2.04	630.0	8.4	153.0
5-10-72	1415-1615	288	106.4	18.5	0.17	2.40	46.8	10.0	11.23
5-17-72	0950-1126	328	62.2	11.6	0.19	2.03	150.0	5.9	51.61
	1135-1438	278	97.2	14.5	0.15	2.05	179.7	8.6	41.88
	1445-1545	338	107.5	14.9	0.14	2.06	185.6	9.6	39.83
	1600-1645	336	68.2	14.6	0.21	2.07	194.8	9.2	43.83
	1655-1745	333	48.2	13.0	0.27	2.09	204.0	9.9	43.07
5-25-72	1300-1610	406	59.2	15.1	0.26	1.89	172.3	8.7	37.43
6-5-72	1350-1600	351	109.3	10.1	0.09	2.09	54.2	9.8	11.56
6-9-72	1100-1230	409	34.6	11.0	0.32	1.96	370.0	6.1	118.89
	1237-1400	352	24.2	8.6	0.36	1.97	388.5	6.5	119.76
	1404-1531	408	23.6	8.0	0.34	1.98	401.5	11.7	67.99
	1538-1708	405	13.0	5.6	0.43	1.99	419.3	10.0	83.44
6-15-72	1440-1525	245	29.2	5.5	0.19	2.15	187.1	9.2	43.70
6-21-72	1037-1255	243	36.7	5.7	0.16	2.01	55.4	6.6	16.87
	1304-1407	242	32.7	8.4	0.27	2.02	64.0	8.6	15.03
	1420-1531	399	29.1	4.8	0.16	2.02	72.6	8.6	17.05
6-22-72	1400-1456	427	32.1	4.4	0.14	1.97	201.8	5.3	75.01
	1506-1735	397	23.7	3.8	0.16	1.99	218.7	6.3	69.08
6-28-72	0712-0814	250	79.1	10.8	0.14	2.05	416.1	2.9	294.14
	0845-1029	251	94.7	10.7	0.11	2.06	419.2	6.6	130.84
	1040-1200	253	101.8	13.0	0.13	2.09	441.0	8.4	109.73
	1210-1345	254	146.3	14.8	0.10	2.09	460.0	9.3	103.38
	1350-1538	398	106.2	12.6	0.12	2.09	472.3	10.2	96.78
	1553-1757	400	40.5	5.2	0.13	2.09	483.7	8.6	117.95
8-30-72	0807-1008	256	167.0			1.89	-33.6	7.3	
	1045-1320	258	203.3			1.89	-54.0	6.4	
	1327-1550	259	141.7			1.89	-63.3	9.1	
9-6-72	1400-1500	249	97.8			2.29	80.3	10.3	17.85
	1505-1733	264	53.8			2.26	89.4	8.9	22.70
10-11-72	0948-1248	581	104.81	14.92	0.14	1.89	15.0	3.0	9.45
	1259-1559	592	81.79			1.89	39.8	7.5	9.83
	1611-1913	591	36.07	6.44	0.18	2.00	79.0	9.5	16.63
	1920-2220	520	20.29	6.35	0.31	1.89	111.0	6.9	30.40
	2227-0125	521	20.17			1.89	134.0	4.0	63.32
10-12-72	0130-0410	522	80.91	14.45	0.28	1.89	144.0	4.6	59.17
	0420-0750	266	109.30	14.41	0.13	1.89	152.0	2.9	99.06
	0800-1130	262	169.02			1.89	8.0	2.4	6.30

samples had a lower C"/C ratio representing vertical mixing with air over the land and the entrainment of dust or other continental aerosols.

The analytical data for the El Segundo 46-meter level samples are summarized in Table IV through the 28th of June. These data, along with the analysis of the Hawthorne data and the results from the Lennox air pollution monitoring station in Table V were used in the assessment of the reactions presented in eqs. (1)-(3). These results will be discussed in a later section.

Table IV

SUMMARY OF CHEMICAL DATA - EL SEGUNDO

Date	Filter	Time	RH (%)	NO_3^- (μmoles/m^3)	Cl^- (μmoles/m^3)	NO_3^-/Cl^-
4-19	285	1513-1621	65	0.051	0.379	0.14
	284	1625-1800	65	0.094	0.231	0.40
4-25	283	1040-1212	69	0.124	0.355	0.35
5-4	279	1200-1325	67	0.089	0.187	0.47
	287	1330-1455	70	0.066	0.134	0.49
	281	1500-1635	70	0.057	0.120	0.47
5-5	289	1745-1950	70	0.044	0.091	0.49
5-10	287	1500-1650	70	0.093	0.181	0.52
5-17	355	1305-1425	78	0.155	0.041	3.75
	329	1439-1519	78	0.097	0.106	0.84
	330	1524-1631	80	0.104	0.113	0.93
	331	1635-1745	81	0.079	0.109	0.71
5-24	353	1500-1630	68	0.073	0.214	0.33
5-25	407	1435-1530	58	0.229	0.202	1.13
6-5	350	1525-1645	73	0.126	0.121	1.03
6-9	401	1140-1250	72	0.087	0.260	0.34
	402	1305-1423	70	0.077	0.147	0.52
	403	1431-1530	70	0.044	0.102	0.43
	404	1537-1643	72	0.043	0.106	0.41
6-15	244	1630-1715	70	0.019	0.070	0.27
6-22	426	1334-1535	68	0.013	0.052	0.25
6-28	396	0948-1030	75	0.238	0.065	3.66
	424	1500-1630	72	0.110	0.037	2.96
	525	1635-1750	72	0.101	0.049	2.06

Table V

SUMMARY OF CHEMICAL DATA - EL NIDO

Date	Filter	Time	RH (%)	T (°C)	H_2O (Partial Pressure, atm)	NO_x (pphm)	NO (pphm)	HNO_3 (μmoles/m^3)	NO_3^- (μmoles/m^3)	Cl^- (μmoles/m^3)	NO_3^-/Cl^-
4-14	291	1350-1622	54	16.1	0.0101	6.9	5.3	0.021	0.113	0.097	1.17
	290	1626-1738	52	15.6	0.0093	6.7	6.5	0.017	0.102	0.157	0.65
4-25	280	1215-1320	52	19.4	0.0116	5.0	1.2	0.029	0.233	0.264	0.87
5-4	324	1030-1229	56	20.3	0.0133	4.5	3.0	0.017	0.076	0.062	1.21
	321	1241-1414	53	20.8	0.0131	5.5	3.5	0.021	0.014	0.033	0.42
	276	1420-1550	53	19.4	0.0121	4.3	3.7	0.013	0.054	0.107	0.51
	277	1558-1735	53	18.4	0.0111	5.0	5.9	0.013	0.044	0.072	0.61
5-5	286	1825-1915	68	14.7	0.0111	2.0	1.1	0.008	0.055	0.155	0.35
5-10	288	1415-1615	64	21.0	0.0160	4.0	2.0	0.019	0.126	0.162	0.78
5-17	328	0950-1126	51	20.6	0.0125	4.0	4.0	0.012	0.102	0.078	1.30
	278	1135-1438	51	21.2	0.0131	4.0	2.3	0.016	0.116	0.109	1.06
	338	1445-1545	52	21.8	0.0137	4.8	2.5	0.020	0.198	0.032	6.19
	336	1600-1645	63	20.6	0.0154	4.0	4.0	0.013	0.130	0.099	1.31
	333	1655-1745	70	18.3	0.0143	3.7	3.7	0.012	0.012	0.079	1.56
5-25	404	1300-1630	55	20.4	0.0133	4.4	3.6	0.015	0.067	0.166	0.41
6-5	351	1350-1600	69	22.8	0.0194	3.2	1.5	0.017	0.138	0.017	8.14
6-9	409	1100-1230	90	17.8	0.0183	5.0	2.0	0.028	0.102	0.069	1.48
	352	1237-1400	68	21.7	0.0177	4.6	2.6	0.021	0.057	0.076	0.76
	408	1404-1531	70	20.8	0.0172	4.7	2.0	0.025	0.067	0.063	0.98
	405	1538-1708	73	19.7	0.0168	4.6	3.6	0.018	0.036	0.050	0.72
6-15	245	1440-1525	68	22.2	0.0177	1.0	5.0	0.002	0.025	0.060	0.42
6-21	243	1037-1255	53	27.2	0.0184	4.1	4.1	0.014	0.047	0.041	1.15
	242	1304-1407	58	23.9	0.0173	5.0	4.6	0.018	0.072	0.060	1.19
	399	1420-1531	57	22.8	0.0159	5.0	5.0	0.016	0.026	0.047	0.55
6-22	427	1400-1456	54	23.4	0.0156	5.1	6.1	0.015	0.024	0.045	0.53
	397	1506-1735	56	22.2	0.0154	3.8	6.6	0.009	0.035	0.024	1.41
6-28	250	0712-0834	82	18.9	0.0179	5.5	3.7	0.003	0.100	0.069	1.45
	251	0845-1029	70	21.9	0.0186	4.1	4.1	0.014	0.114	0.051	2.24
	253	1040-1200	61	24.0	0.0183	7.8	5.8	0.039	0.153	0.049	3.13
	254	1210-1345	67	23.9	0.0202	6.9	3.3	0.037	0.187	0.043	4.34
	398	1358-1538	73	21.9	0.0186	4.0	2.7	0.017	0.143	0.065	2.20
	400	1553-1757	76	21.2	0.0195	3.8	2.8	0.016	0.063	0.018	3.49

VI. DISCUSSION

A. Diurnal Cycle

1. Meteorological Conditions

The diurnal onshore-offshore flow of air is the most common pattern along the coast of southern California. As mentioned earlier, a strong onshore influx of marine air onto the land during the day is followed by a weak reverse flow at night. Data that characterize portions of this cycle are summarized in Attachment A (Green, 1972). In order to collect representative data throughout a complete cycle, meteorological data were collected throughout a 48-hour cycle on 10-12 October 1972. Aerosol samples were collected and analyzed over the second 24 hours of this period.

The air flow pattern is diagrammed in Figure 3 starting at 1000 on 10 October. The total net onshore wind-run from that time until 1000 on 12 October is charted with specific milestones indicated by arrows.

Onshore flow during the afternoon of 10 October persisted until about 2100 hours followed by a brief calm period. Offshore flow started about 0130 and continued until 0830. By 1430 that afternoon, all the polluted continental air that had moved offshore the previous evening had been ventilated inland and was followed by relatively clean marine air until calm conditions set in about 0200 the following morning.

2. Vertical and Horizontal Transport of Aerosols

The collection of filter samples started at about 0900 at each of the three sampling sites, the 46-meter and 12-meter levels at El Segundo and the 6-meter level at Hawthorne.

In Figure 4, the total aerosol concentration at each of the sites is plotted against time of day.

Shortly after the end of the offshore flow at 0830 on 11 October, the concentration of aerosol at the 12-meter level at El Segundo was approximately 4 times the concentration at the 46-meter level. Reference to the C"/C values in Tables I

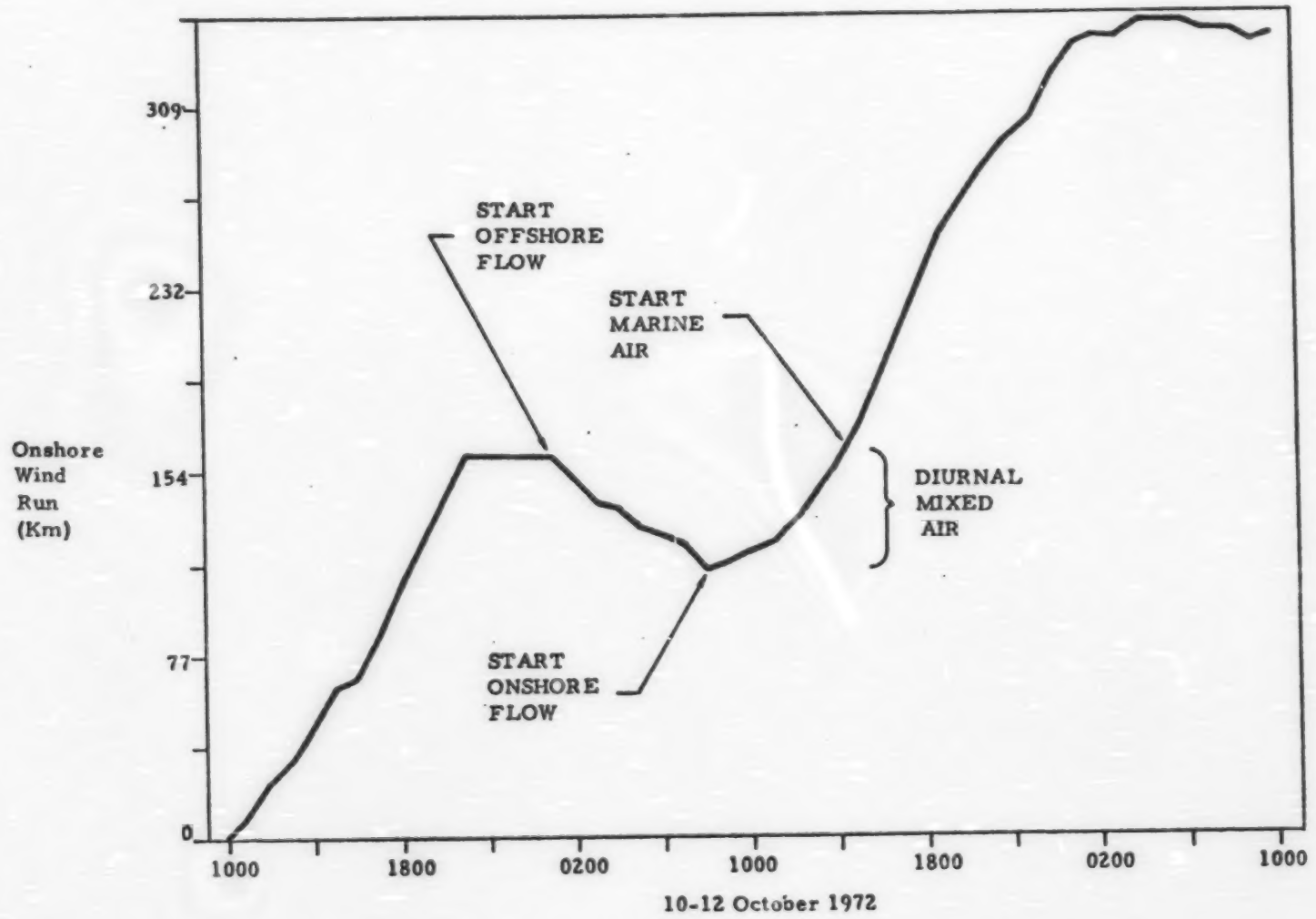

Fig. 3. TYPICAL AIR FLOW PATTERN NEAR EL SEGUNDO

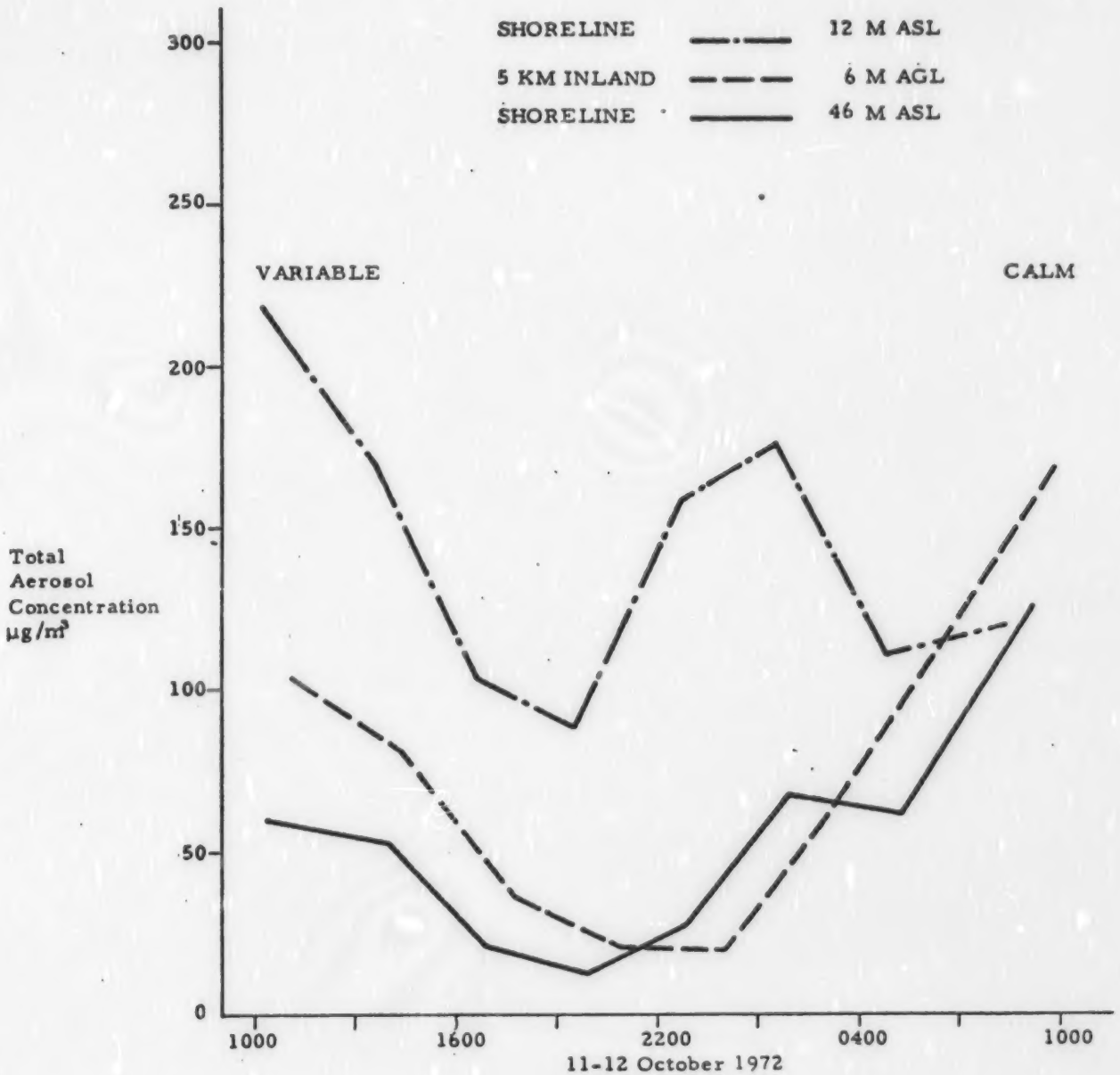

Fig. 4. VERTICAL MIXING AND HORIZONTAL TRANSPORT OF AEROSOL DURING DIURNAL CYCLE

and II indicate that chemically these samples were not very different. An enrichment with respect to surf spray particles is noted at the lower level due to double passage over the surf line, once as the air moved seaward and second as it moved inland just prior to sampling. The sharp concentration gradient between the two levels implies little vertical mixing of surf spray and land derived aerosols.

Throughout the afternoon and early evening the stratification persisted. By 2000 the total concentration at the 12-meter level had decreased by a factor of 2.5 while at 46 meters the decrease was over a factor of 4.0. Higher surface winds and associated sea spray combined with dilution of the more seaward polluted air resulted in an increase in the C"/C ratio at 12 meters. At 46 meters this ratio remained approximately the same.

After the passage of the seaward "smog front" or diurnal mixed air (Fig. 3) at about 1800-2000 hours, the concentration of aerosol at both levels started to increase. The sharp increase at the lower level would imply a sudden influx of salt-charged air from the open ocean, air which had received a large component of salt particles due to long exposure to the sea surface and short exposure to high midafternoon winds (up to 12.5 mph). This increase in aerosol loading is reflected similarly at the upper level due to vertical mixing. Regretfully, none of the late evening samples was analyzed chemically to verify an increase in salt. Evidence from analysis of other samples collected under similar conditions does confirm this increase in salt. Previous studies (Green, 1972) indicated that most of the overall increase in mass was due to large (more than 3 μm) salt spray particles.

After the onshore wind declined in the early morning of the 12th, salt values at both levels decreased. Vertical mixing and the wash of polluted air back and forth over the shoreline tended to bring the concentration and composition of the marine layer into a degree of harmony.

Results at Hawthorne 5-Km inland reflect the trends at El Segundo. The total aerosol concentration during the passage of the mixed diurnal air fell between the surf-enriched values of the 12-meter level and the more homogeneous values at the 46-meter level. Initially, between 1000 and 1900,

C"/C ratios at Hawthorne were 1/2 to 1/3 the shoreline values, implying the fallout of salt. The aerosol mixture arriving at Hawthorne reflected a mixture of the diurnal air and a locally derived pollution or ground dust component.

After the passage of the diurnal air, the C"/C values at Hawthorne increased from 0.14-0.18 to 0.28-0.31. These data support the previous implication that the oceanic air and associated sharp increase in total aerosol at the coast is due to sea salt.

At about 0100, the total aerosol concentration increased rapidly at Hawthorne. This increase was accompanied by calm conditions and a drop in the C"/C ratio implying a decline in salt transport coupled with a buildup of aerosols from local pollution sources.

The distribution of salt vertically and horizontally as a function of wind speed can be summarized in the following Table VI abstracted from Tables I, II, and III.

Table VI

DISTRIBUTION OF SALT

Time	Onshore Wind Speed (mph)	Equivalent Sea Salt C" $\mu g/m^3$ El Segundo 46-m	El Segundo 12-m	Hawthorne 6-m
0900-1200	3.0	21	92	15
1800-2100	7.0-11.0	4	46	6
0300-0700	3.0-4.0	16	38	14

Under nearly calm conditions, vertical mixing is most pronounced and, with slight onshore winds, air containing a heavy charge of salt can blanket the near coastal regions. The total inland salt flux (concentration times wind speed) remains about the same under winds of 3 to 11 mph, but at the higher winds, more salt is derived from the near surface boundary layer. These larger precipitable particles contribute to a heavier fallout of salt along the coast.

3. Summary

Under conditions of moderate onshore or offshore wind, the aerosol loading of the coastal marine atmosphere becomes relatively stratified. Sharp vertical gradients exist with the lower levels near the ground or sea surface becoming enriched in either pollution or sea spray particles. Under moderate onshore winds (10-12 mph) large salt particles are transported inland 5 or more kilometers in measurable quantities. At lower wind speeds and particularly under near calm conditions, salt is mixed vertically, reaching concentrations which exceed values measured under strong onshore wind conditions.

B. Persistent Onshore Flow

1. Meteorological Conditions

The majority of the dates between April and September 1972 were selected for meteorological conditions which favored persistent onshore flow of air. These conditions afforded the best opportunity to sample air with an implied origin beyond local continental influences. This search for air containing a pure marine aerosol proved futile. Only one set of samples collected on 9 June 1972 contained little or no altered or mixed marine and continental aerosol.

The purity of marine air is normally expected to increase with the source distance and the magnitude of the sea state. However, the total aerosol and equivalent sea salt concentrations measured at the El Segundo 46-meter level under persistent onshore flow conditions indicate that this assumption may be in error.

To account for the existence of salt-deficient aerosol at offshore distances in excess of 300 to 500 miles, the meteorology was examined on the days when samples were collected. The basic long range trajectory patterns were similar for all these dates. A high over the coast of Washington was feeding air in a clockwise direction out over the ocean and back inland toward a thermal low over the California-Arizona-Nevada desert. The intensity of the air flow toward the low caused persistent onshore winds for several consecutive days along the California coast.

The exact source of the non-marine aerosols sampled at El Segundo cannot be determined without more detailed data on winds at sea. However, the meteorology illustrates the possibility that, through large scale air circulations, continental aerosols can persist in air which appears to originate from considerable distances at sea. Considering that several days (approximately five) were required for the air to flow from the northwestern U. S. to the Los Angeles area, the duration of continental aerosols throughout this time period may be an indication of poor scavenging or dilution mechanisms over the ocean.

2. Aerosol Composition as a Function of Source

The data in Table I for total aerosol and equivalent sea salt concentration at the El Segundo 46-meter level are displayed in Figs. 5 and 6 as a function of the source-production-ventilation parameter $\overline{SD}/V_L$. Air originating near the coast or having relatively short exposure to the marine environment had high concentrations of aerosols. This concentration dropped off to a minimum value at about 50 to 60 on the $\overline{SD}/V_L$ scale. Similarly, the equivalent sea salt concentration reached a minimum around the same value.

Beyond the minimum, the total aerosol concentration increased more rapidly than C", implying an aerosol source other than sea spray. The relationship between C" and C is best illustrated in Fig. 7 where the ratio C"/C is plotted against $\overline{SD}/V_L$.

Near shore the aerosol is rich in chloride, and this chloride component makes up nearly 60 percent of the total concentration. Little or no nitrate is observed. Further offshore at exposures approximating 20 hours, the salt component drops dramatically and much of the chloride is lost at the expense of nitrate. This region between 0 and 20 on the $\overline{SD}/V_L$ scale represents the offshore-onshore cyclic diurnal circulation.

Air that passes the shoreline and returns on the onshore breeze will be rich in pure sea spray particles from the surfline. Little time is available for fallout of the larger, chloride-rich aerosols. Reactions between NO_2 and moisture in the particles are minimal.

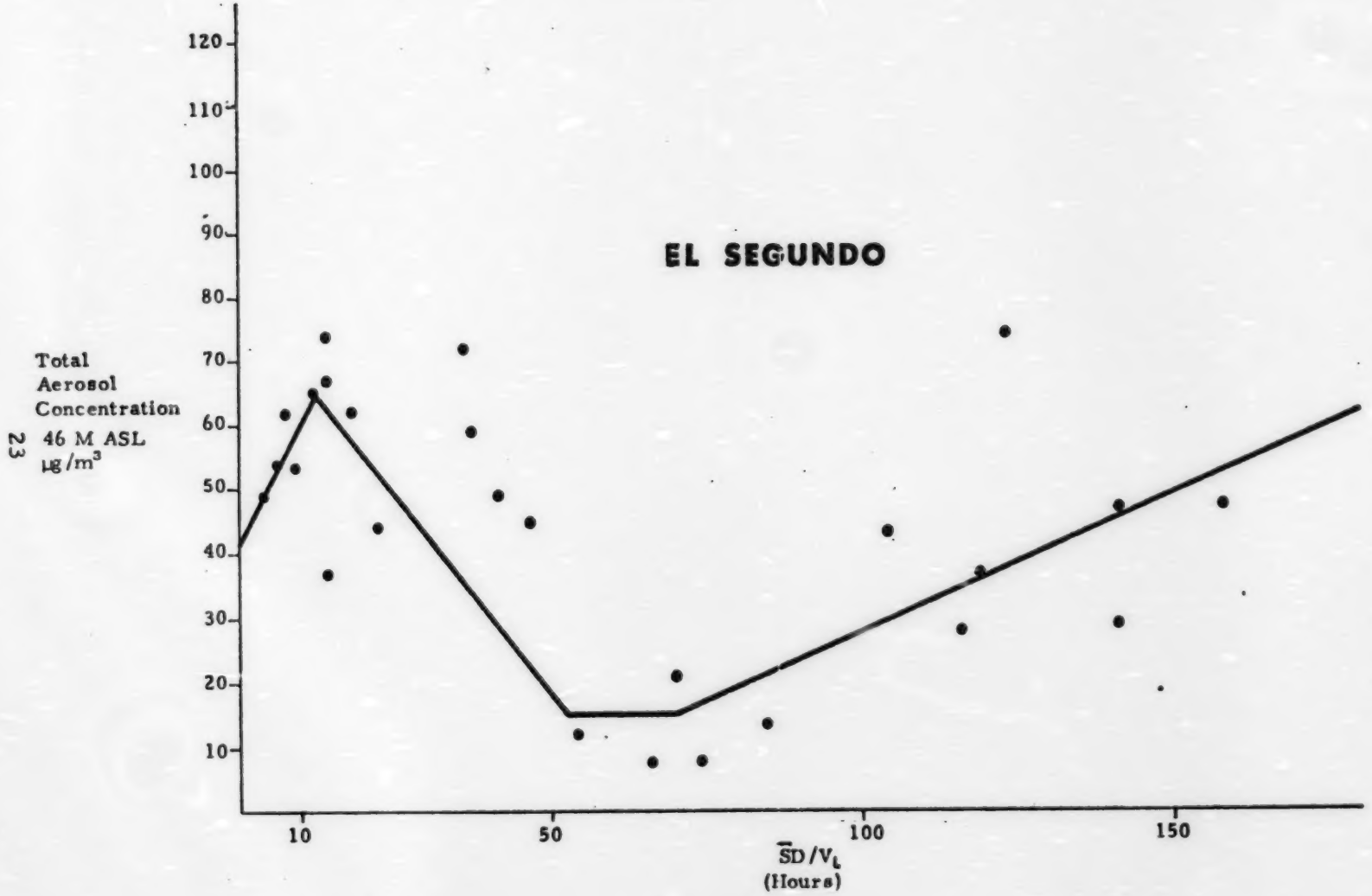

Fig. 5. TOTAL AEROSOL CONCENTRATION 46 METERS ABOVE SEA LEVEL AS A FUNCTION OF EXPOSURE TO MARINE ENVIRONMENT

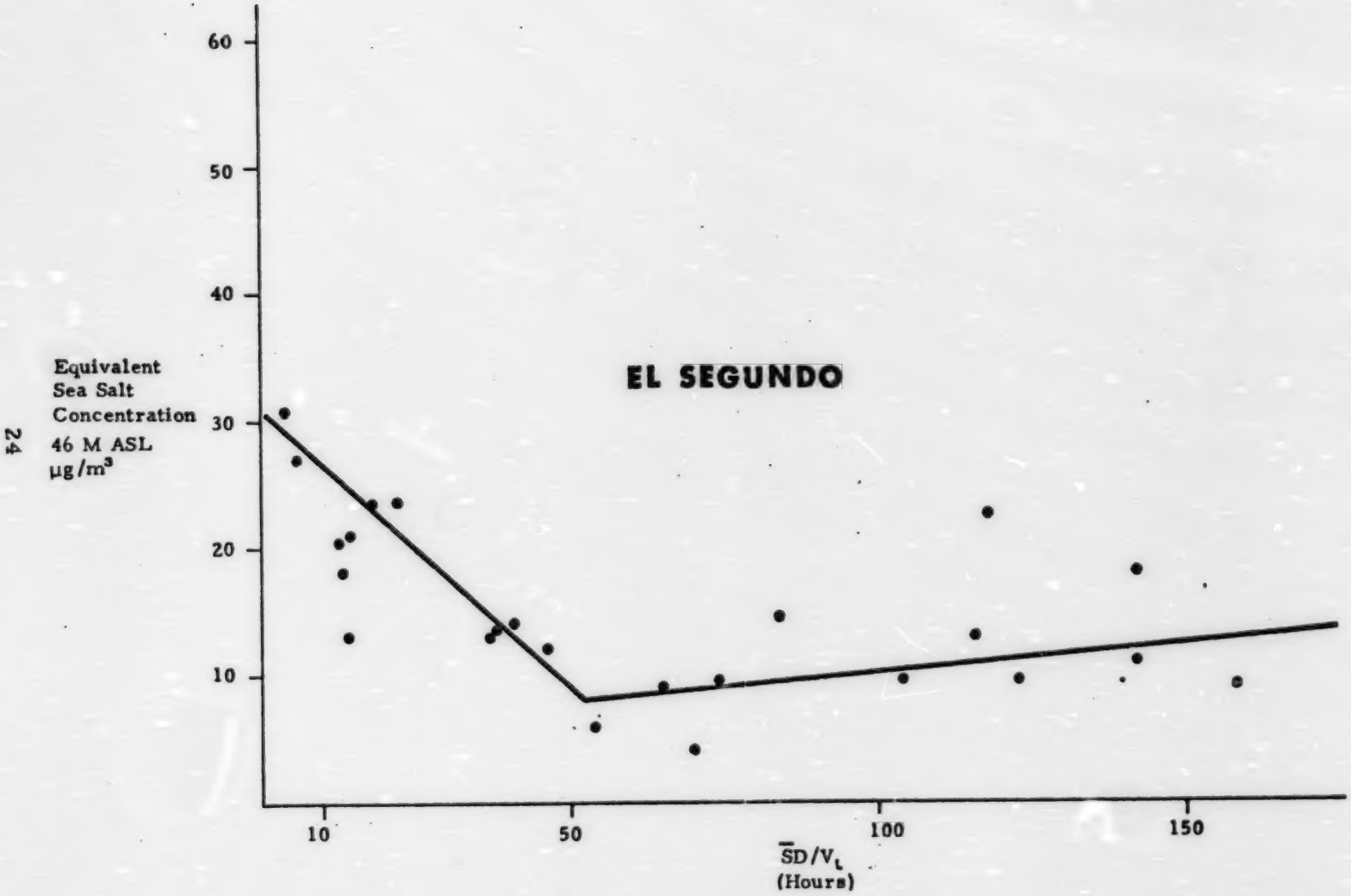

Fig. 6. EQUIVALENT SEA SALT CONCENTRATION AT 46 METERS ABOVE SEA LEVEL AS CALCULATED FROM Cl^- AND NO_3^-

As the polluted air is exposed to the marine environment for longer periods of time, the larger surf particles precipitate, and more small particles are generated at the ocean surface. The opportunities and the time available for reactions between NO_2 and these particles increases. A minimum is reached near the seaward edge of the polluted air where most of the aerosol consists of residual pollution particles and reacted marine aerosols rich in nitrate.

Air derived from regions beyond the influence of local diurnal circulation should contain higher and higher percentages of sea salt aerosol. This trend is confirmed by the gradual increase in marine aerosol character observed in Fig. 7. Nitrate persists in the aerosol, but the percentage of non-salt particles decreases significantly up to an $\overline{SD}/V_L$ value of about 70. If the trend continued and the air became more and more marine in character, C"/C should approach a value of 1.0.

At 70 the trend was reversed, and the aerosol became more and more continental in character. Subsequently an analysis of the meteorology was performed for several of the days with high $\overline{SD}/V_L$ values and the air flow from the Pacific northwest to a thermal low east of Los Angeles was identified as the cause.

Some latitude dependence for the formation of nitrate aerosols in the marine environment can be inferred from Fig. 7. As the source of the air approached more southerly latitudes, the nitrate increased. However, many factors including history prior to inclusion in the sweep from the Pacific northwest to Los Angeles and actual exposure time in a nitrogen dioxide enriched environment should be examined.

3. Summary

Under near-shore conditions, the maritime aerosol appears to be enriched in chloride-containing salt spray. As the source distance and exposure time of polluted air over the ocean increases, surf spray particles are precipitated and nitrogen dioxide reactions convert much of the remaining salt to nitrate aerosols.

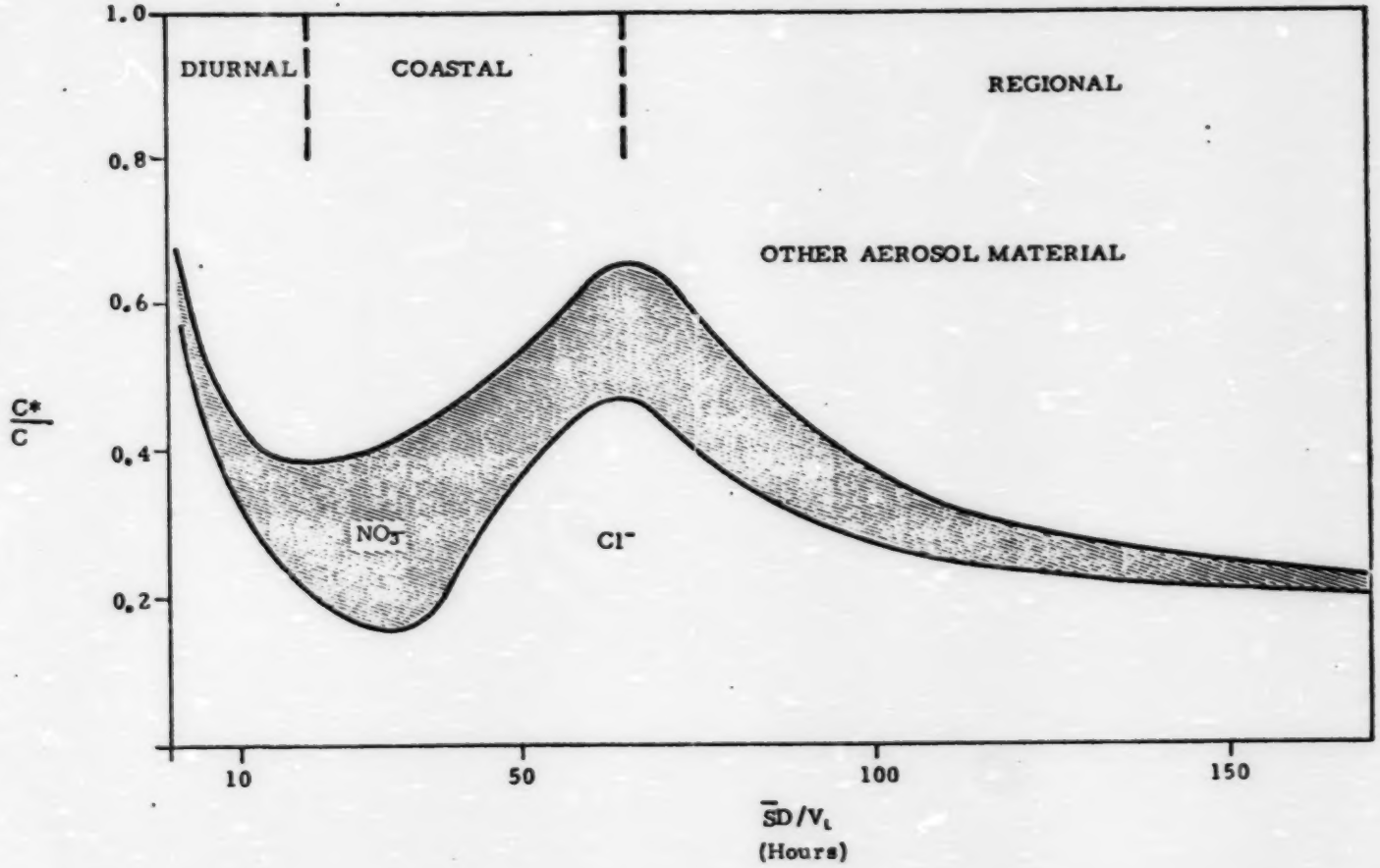

Fig. 7. RATIO OF EQUIVALENT SEAL SALT TO TOTAL AEROSOL AS A FUNCTION OF AIR SOURCE

C* = Equivalent sea salt calculated from Cl^- or Cl^- + NO_3^-

If the source is beyond the localized circulation pattern along the coast, most of the non-salt or pollution aerosol is replaced by particles resembling purer marine aerosols. Nitrate generating reaction mechanisms are still evident.

Large scale regional flow patterns can cause masses of continental air to be injected into the marine environment. This air retains a strong continental character and high non-salt particle count after marine exposures in excess of five days.

C. Inland Transport - 5 Km El Segundo to Hawthorne

1. Aerosol Composition as a Function of Source

The data collected on filters at Hawthorne, 5 Km inland from El Segundo, was summarized in Table III. Each sample was collected as close as possible in time to a comparable sample at the El Segundo 46-meter level. These data are presented in Fig. 8.

The total aerosol concentration at Hawthorne, as seen in Fig. 8, was widely scattered out to an $\overline{SD}/V_L$ value of 70. Many of the higher concentrations occurred at winds above nine to ten miles per hour and probably reflect a combination of diurnal polluted air and wind-blown dust entrained between El Segundo and Hawthorne. Beyond 70 the trend increased slowly reflecting similar observations summarized in Fig. 4 for El Segundo.

The equivalent sea salt aerosol concentration, C", at Hawthorne (Fig. 9) appeared to be independent of the source parameter $\overline{SD}/V_L$. Values were confined within a region around 10 $\mu g/m^3$. Beyond a value of 70 on the $\overline{SD}/V_L$ scale, the ratio of C"/C was similar, but slightly lower than C"/C at El Segundo. Under the influence of persistent onshore winds, much of the ground debri may have been winnowed, resulting in a minimal entrainment of dust or other pollutants between El Segundo and Hawthorne.

In general, the total and equivalent sea salt concentrations at El Segundo and Hawthorne under persistent, but moderate (less than 7-8 mph), onshore winds are nearly identical. The entrainment of dust and deposition of small oceanic salt particles are minimal.

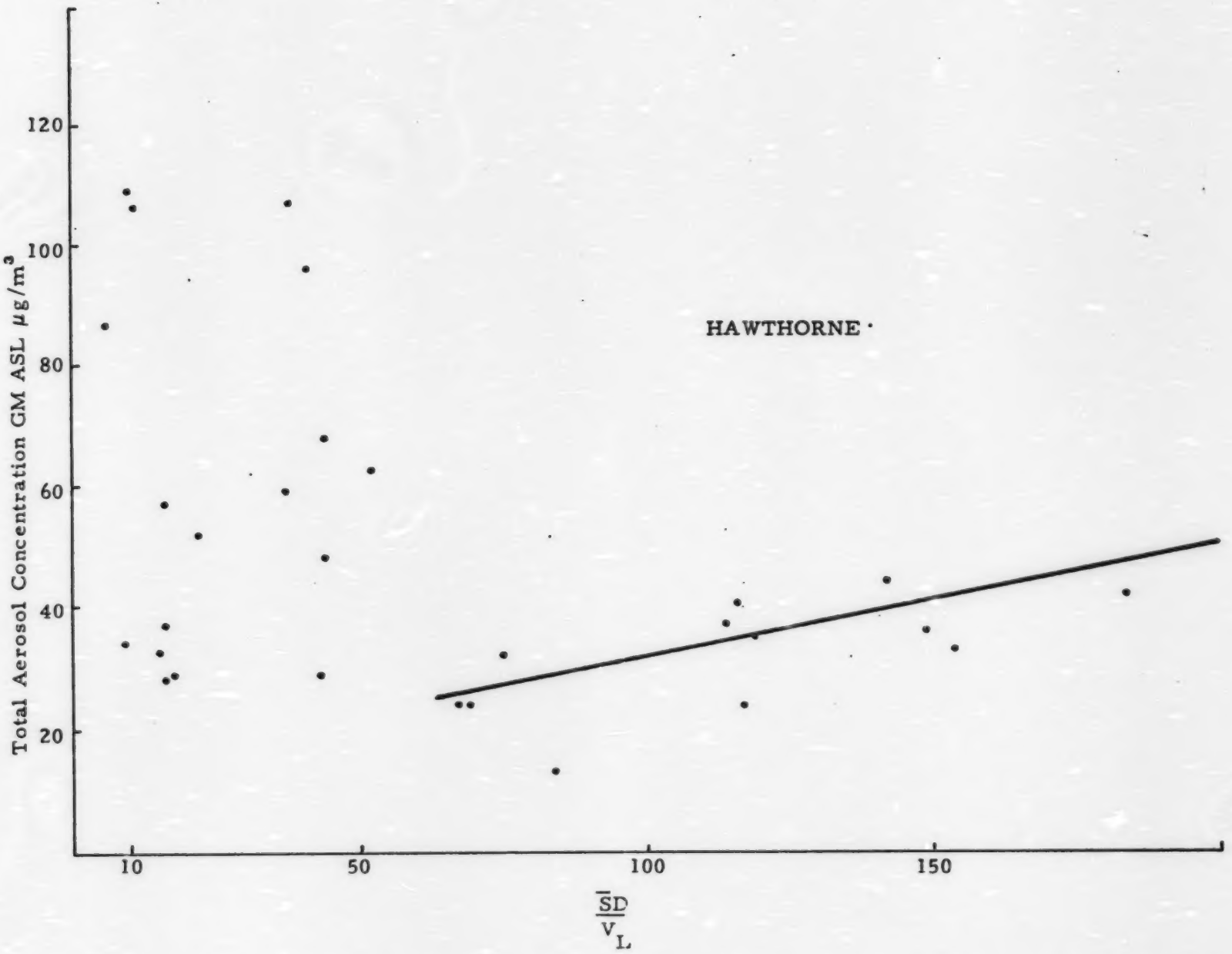

Fig. 8. TOTAL AEROSOL CONCENTRATION - C AT HAWTHORNE 6 METERS ABOVE GROUND LEVEL

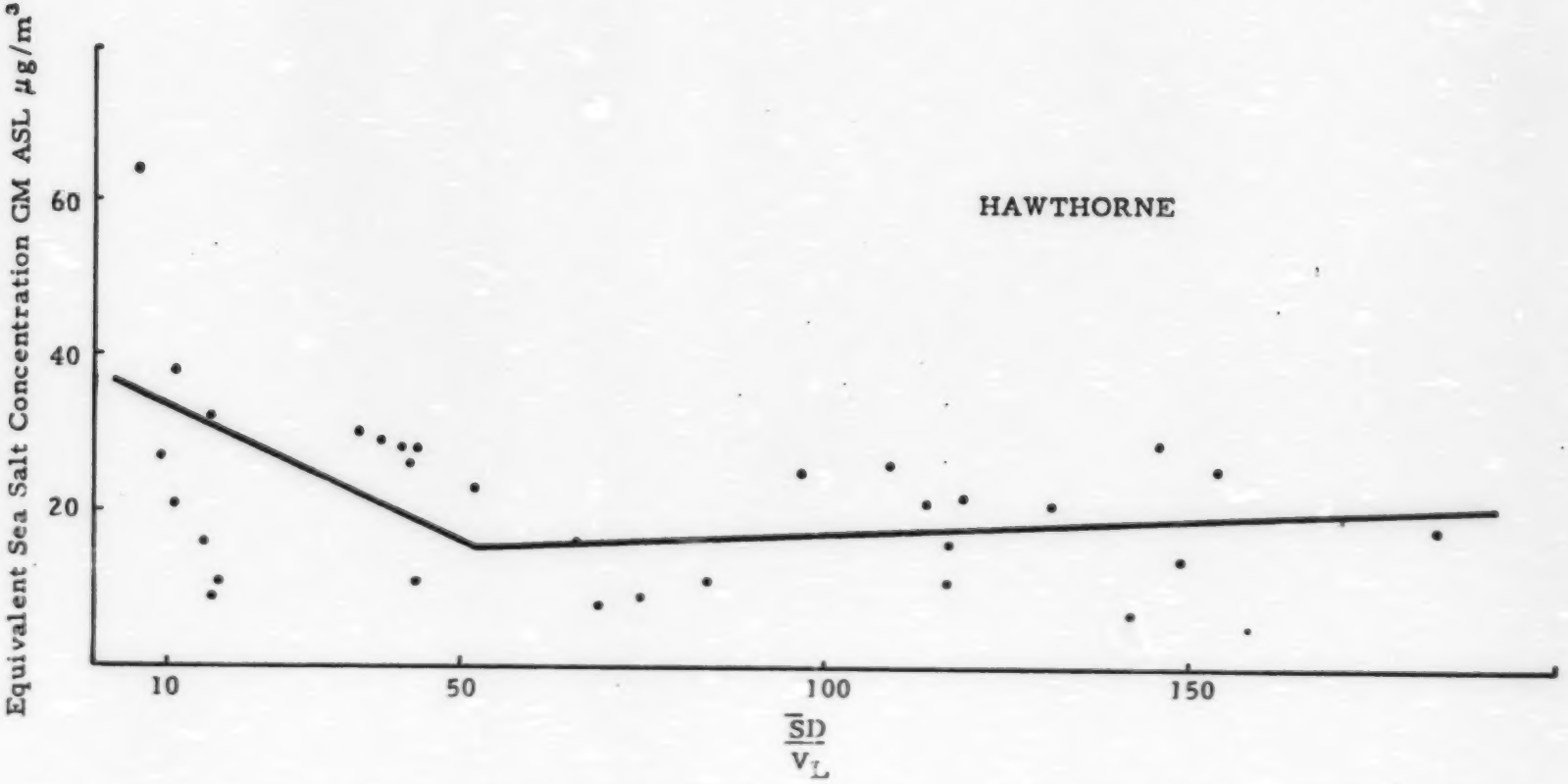

Fig. 9. EQUIVALENT SEA SALT CONCENTRATION - C'' AT HAWTHORNE 6 METERS ABOVE GROUND LEVEL

2. Transport of Salt and Dust

Results of the 24-hour diurnal study indicated that the total flux of salt at Hawthorne remained nearly constant regardless of wind speed. The principal change was a shift to larger sea or surf spray particles and an associated decrease in the quantity of salt mixed vertically as the wind increased.

When the total aerosol concentration at Hawthorne is compared to contemporaneous samples taken at El Segundo, the wide scatter of data in Fig. 8 can be explained. As mentioned earlier, many of the higher concentrations in Fig. 8 occurred at wind speeds of nine to ten mph.

In Fig. 10, the ratio of total aerosol concentration, C_H, at Hawthorne to the concentration, C_{ES}, at El Segundo is plotted against wind speed. Below wind speeds of seven to eight mph, the ratio C_H / C_{ES} is nearly one, implying little change in concentration due to entrainment or deposition between El Segundo and Hawthorne. Above eight mph, the concentration at Hawthorne increases sharply, reaching values twice the upper level values at El Segundo. The composition of the aerosol can be inferred from a comparison between Figs. 8 and 9 where only a slight increase in equivalent sea salt was noted in the same source regime. Most of the increased aerosol loading at wind speeds above eight mph is due to entrained dust or other continental aerosols.

The relative importance of dust entrainment compared to large particle salt transport can be seen when Fig. 11 is compared to Fig. 10. In Fig. 11, the same contemporaneous values for equivalent sea salt at El Segundo and Hawthorne are plotted as a ratio against the wind speed. At lower wind speeds, the ratio C''_H/C''_{ES} is less than one. Above eight mph the trend is upward, but less dramatic than the increase shown in Fig. 10.

3. Summary

Under persistent onshore winds, the composition and relative concentrations of equivalent sea salt and total aerosol at the shoreline and at a point 5 Km inland are nearly identical. This composition and concentration appears to be independent of wind speeds below eight miles per hour.

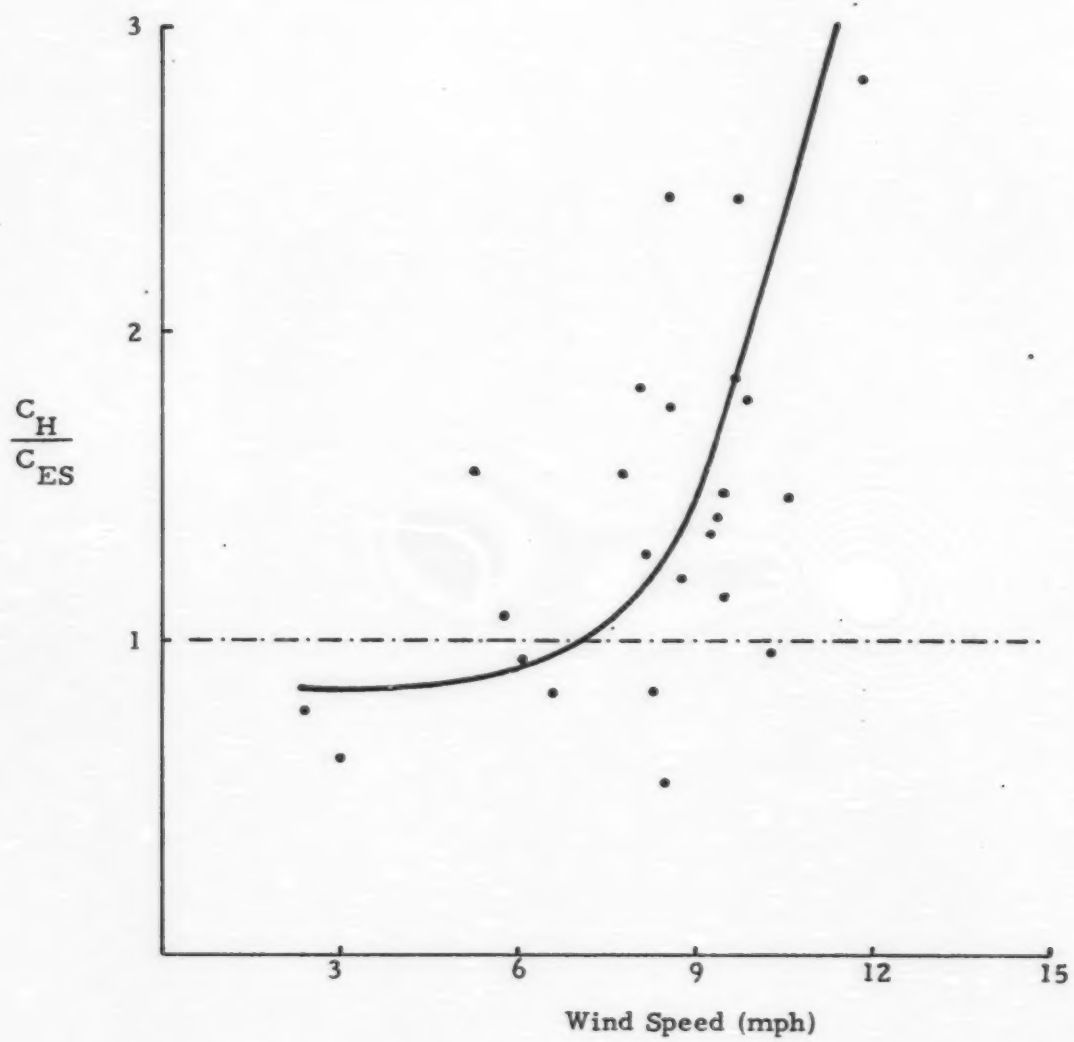

Fig. 10. SURF SPRAY AND GROUND DUST COMPONENT ARRIVING AT HAWTHORNE AS A FUNCTION OF TRANSPORT WIND SPEED AND TIME OF DAY

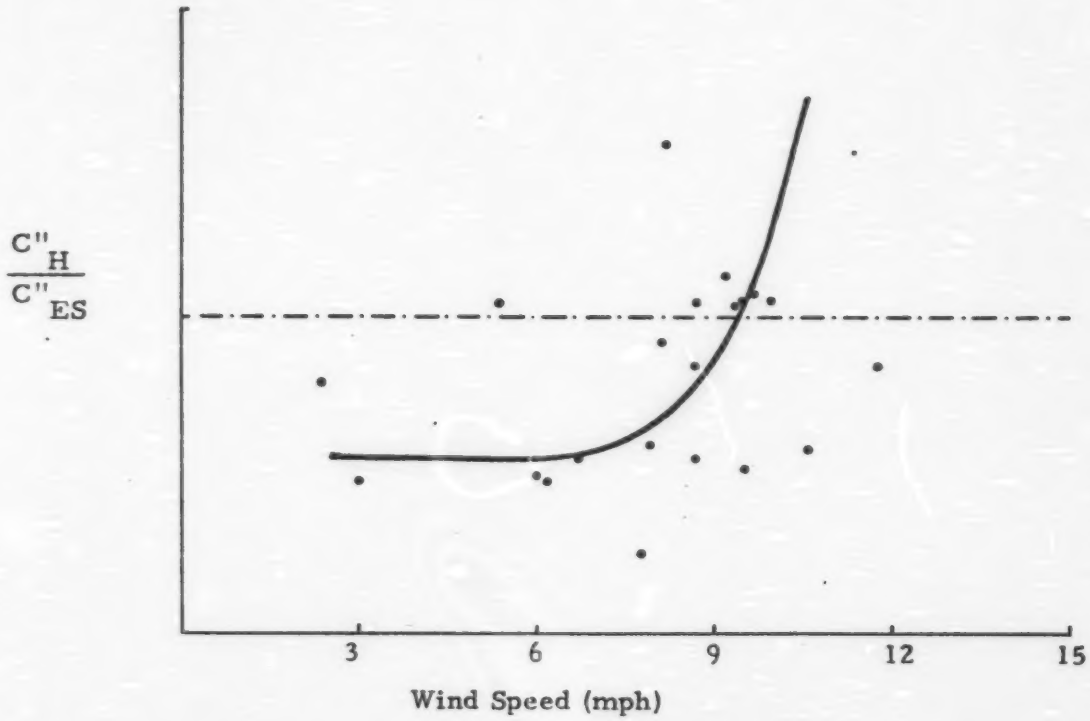

Fig. 11. EQUIVALENT SEA SALT ENRICHMENT AT HAWTHORNE AS A FUNCTION OF TRANSPORT WIND SPEED

Above eight miles per hour and particularly under conditions of diurnally fluctuating onshore-offshore winds, the entrainment of continental dust over a five Km path can result in a 2 to 3 fold increase in overall aerosol concentration. A smaller increase in the salt concentration can result from the transport of salt spray particles from the surfline.

D. Nitrate Reactions in the Maritime Aerosol

1. Background

Several mechanisms have been suggested for the formation of nitrate in maritime aerosols. One mechanism involves the reaction of nitrogen dioxide with chloride ion in sea salt aerosols to form at ambient temperatures nitrosyl chloride which is easily hydrolyzed or photolyzed releasing gaseous nitric oxide and chloride.

The mechanism follows the path:

$$2NO_2 + NaCl \rightarrow NaNO_3 + NOCl \qquad (5)$$

with the nitrosyl chloride hydrolyzed according to

$$NOCl + H_2O \rightarrow HCl + HNO_2 \qquad (6)$$

or photolyzed according to

$$NOCl \xrightarrow{h\nu} NO + Cl. \qquad (7)$$

Either route results in the loss of chlorine in the form of hydrogen chloride or chlorine gas.

Robbins, et al., (1959) found evidence that the reaction between sodium chloride aerosol and nitrogen dioxide did not follow this route. With nitrogen dioxide concentrations ranging from 0.1 to 100 ppm and aerosol concentrations from 0.2 to 430 μmoles/m^3, the reaction was rapid, but incomplete, reaching equilibrium in less than 10 minutes. In addition, irradiation of the reaction chamber to photolyze any nitrosyl chloride present had no effect on the equilibrium, and no nitrite was found among the reaction products. Nitrate aerosol was formed when calcium chloride aerosol was substituted for sodium chloride, although moist calcium chloride in bulk did not react with nitrogen dioxide to form nitrosyl chloride.

As a result of their experiments, Robbins, et al., suggested that the first step of the reaction is the hydrolysis of nitrogen dioxide in the gas phase:

$$3NO_2 + H_2O \rightleftarrows 2HNO_3 + NO$$

This reaction had a measured vapor equilibrium constant of

$$K = \frac{HNO_3)^2\ (NO)}{(NO_2)^3\ (H_2O)} = 0.004\ atm^{-1} \qquad (8)$$

at 25 °C. With typical atmospheric water vapor concentrations, a few (3-4) percent of the nitrogen dioxide was converted to nitric acid vapor. If the nitric acid is absorbed on the surface of sea salt aerosols at low humidities, the subsequent reaction would be

$$HNO_3 + NaCl \rightarrow HCl + NaNO_3 \qquad (4)$$

with the release of hydrogen chloride by desorption. With the conversion of nitric acid to nitrate, additional acid would be formed by eq. (2) providing the NO_2 levels in the atmosphere were maintained.

Experimental atmospheres initially prepared from either hydrogen chloride and sodium nitrate or sodium chloride and nitric acid vapor indicated that an equilibrium for reaction (4) is reached with the equilibrium constant K',

$$K' = \frac{(HCl)\ (NaNO_3)}{(HNO_3)\ (NaCl)} \qquad (9)$$

in the range of 2 to 6.

Although all their experiments were carried out with gas and aerosol concentrations considerably higher than would be encountered in the atmosphere, Robbins, et al., postulate that the same reactions would occur, with differences in rate, at the lower concentrations typically found in the atmosphere.

An alternative to the relatively slow and incomplete vapor phase reaction in eq. (2) is the direct solution of nitrogen dioxide in liquid water aerosols according to the equation

$$2NO_2 + H_2O_{Liquid} \rightleftarrows HNO_3 + HNO_2 \qquad (3)$$

Decomposition of the nitrous acid would promote the release of nitric oxide and the production of additional nitric acid.

In the following discussion, reactions between nitrogen oxides and both wet and dry marine aerosols will be examined. Production of nitrate in the aerosol is related directly to relative humidity and the deliquiescent state of the salt.

2. Coastal Aerosols

The chemical data for the samples collected at the 46-meter level at El Segundo were summarized in Table IV. When the NO_3^-/Cl^- ratio for these samples was plotted against relative humidity, as in Fig. 12, the majority of points clustered at an NO_3^-/Cl^- ratio of 0.3 to 0.5. This observation agrees favorably with NO_3^-/Cl^- ratios in giant particles observed near Boston (Junge, 1956); however, some mixing of marine aerosols and continental pollutants containing nitrate could account for the high nitrate values in both cases.

Above 72 percent relative humidity, a rapid increase in the NO_3^-/Cl^- ratio was noted for some of the coastal aerosol samples. This observation suggests a sudden change in the NO_2 conversion to nitric acid and eventually to nitrate as the salt deliquieses to the liquid phase. The calculated equilibrium constant for vapor phase, eq. (2), and liquid phase, eq. (3), support this observation.

$$K_{P_{Vapor}} = 0.0058 \text{ atm}^{-1}$$

$$K_{P_{Liquid}} = 9.3 \times 10^{3} \text{ atm}^{-1}$$

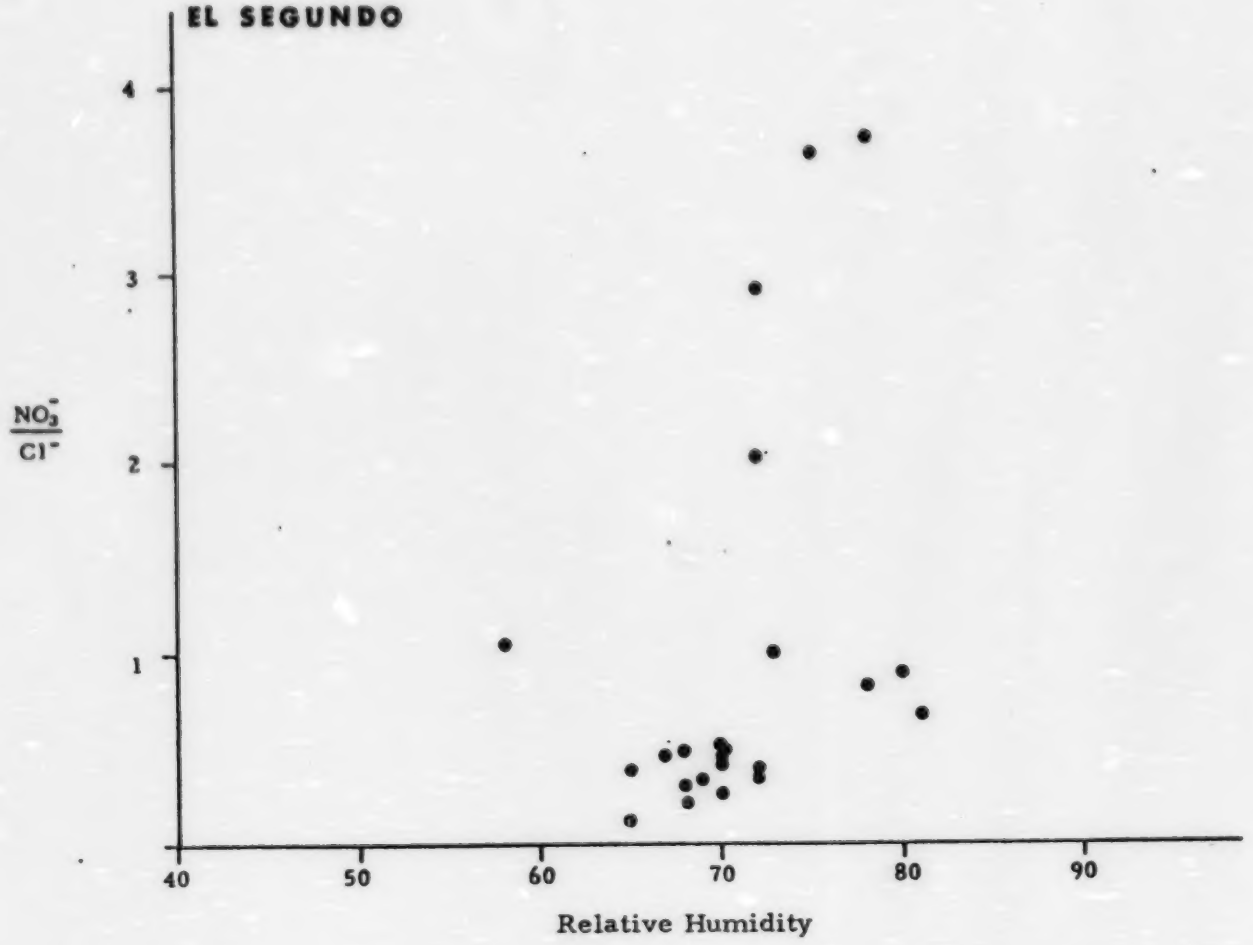

Fig. 12. VARIATION OF NITRATE TO CHLORIDE RATIO AS A FUNCTION OF RELATIVE HUMIDITY

The value of $K_{P_{Vapor}}$ agrees favorably with the value of 0.004 atm^{-1} measured by Robbins, et al., (1959). $K_{P_{Liquid}}$ is basically the solubility of NO_2 in water.

The results of the coastal studies presented in Fig. 12 imply a close relationship between the amount of nitrate measured in the aerosol and the physical state of the marine aerosol. With one exception, all samples collected at relative humidities below 72 percent, where salt particles should be dry, were low in nitrate. Above 72 percent, where the salt deliquiesces to a liquid, the solubility of NO_2 and subsequent reactions along the line of eq. (4) appear to have created high nitrate residues.

3. Inland Aerosols

For the inland aerosol samples, the dependence of the NO_3^-/Cl^- ratio on the nitrogen dioxide and nitric oxide concentrations in continental air was examined by comparing the NO_3^-/Cl^- ratio with the equilibrium nitric acid concentration (HNO_3 equilib.). In order to derive the nitric acid concentration, nitric oxide and nitrogen dioxide data were obtained from records at the air pollution control station at Lennox. This data, presented in Table V, were selected for the same time periods over which aerosol filter samples were collected.

The equilibrium concentration for nitric acid (HNO_3 equilib.) was calculated from the gas data using the appropriate values of K_P for the vapor or liquid phase reaction. These values are plotted in Fig. 13 against the NO_3^-/Cl^- ratio for measurements made at Hawthorne.

Dependence of the results on the phase of the aerosol was again observed. The relative humidity measured at Hawthorne was not a direct indicator of the aerosol phase, but consistently higher NO_3^-/Cl^- ratios were observed on days when the coastal relative humidity exceeded the 72 percent level. Although the inland humidities were usually lower than at the coast, the coastal humidity is a reasonable indicator of the phase of the aerosol when it reaches the inland point. The phase transition for sea salt aerosol from liquid to solid does not occur immediately at 72 percent. Some hysteresis exists which may keep the particles liquid below that point. In extreme cases the humidity may drop as low as 40 percent before solidification

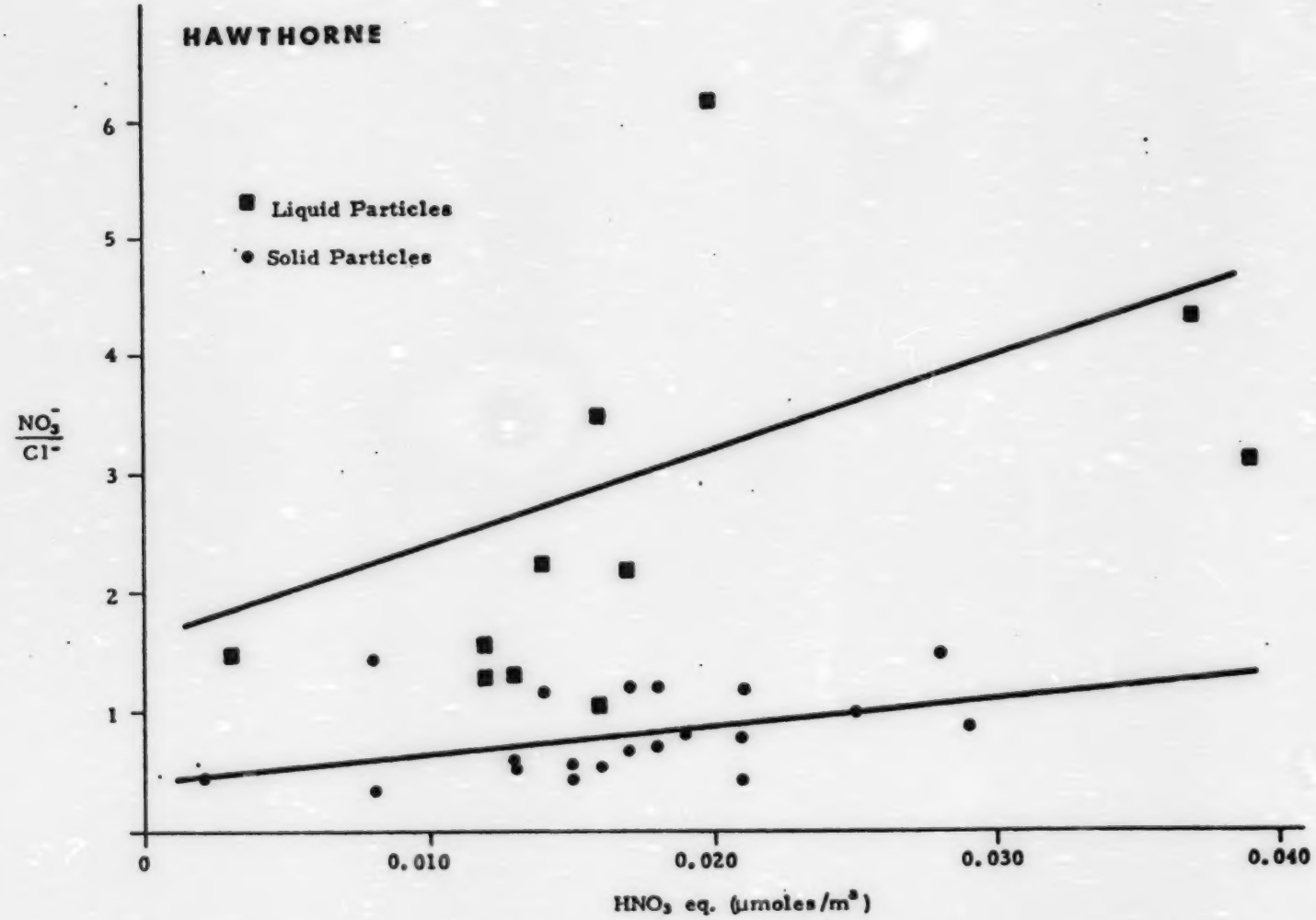

Fig. 13. NITRATE TO CHLORIDE RATIOS AS A FUNCTION OF THE CALCULATED HNO_3 EQUILIBRIUM CONCENTRATION IN AIR AT HAWTHORNE

occurs. All relative humidity measurements at Hawthorne were well above this minimum value.

The data in Fig. 13 grouped fairly distinctly into two sets based on the inferred physical state of the aerosol. The same relationship seen at the coast between the amount of nitrate measured in the aerosol and the presence of a liquid phase was observed at the inland site.

The equilibrium constant, K', was calculated for all the data points, using eq. (9), (HNO_3 equilib.) for (HNO_3), (Cl^-) for (NaCl), and assuming (HCl) = ($NaNO_3$) = (NO_3^-). Average values of K' were 26 and 3, for the liquid and solid aerosol, respectively.

An attempt was made to correlate chlorine loss and nitrate gain between El Segundo and Hawthorne, using pairs of samples collected at approximately the same times. Although generally the NO_3^-/Cl^- ratios were higher at Hawthorne, a clear cut demonstration of nitrate enrichment in the same air parcel could not be achieved with the limited data available. A more detailed study, including the collection of intermediate samples, would be required before a conclusion could be drawn.

VII. CONCLUSIONS

A. Vertical Mixing

As the air along the coast oscillates across the shoreline during periods of diurnal onshore-offshore wind flow, there is a tendency for the air to become enriched with large particles produced in the surf zone. During periods of near calm wind conditions, these particles may mix vertically in excess of 50 meters. As onshore wind flow increases, there is greater horizontal transport and less vertical mixing of the surf zone aerosol at the immediate coast.

B. Source Dependence

Air circulating near the shoreline is enriched in surf spray particles containing high chloride values. At greater source distances, the spray particles are precipitated. Long exposure to nitrogen dioxide enriched air may convert many of the remaining salt particles to nitrate aerosols. Air with apparent sources far offshore often represents massive recirculation of continental air which retains a continental aerosol population after many days over the ocean.

C. Inland Transport

Under near calm conditions, a blanket of surf particle-enriched air may intrude several kilometers inland. As onshore winds increase up to eight miles per hour, the composition and relative concentrations of equivalent sea salt and total aerosol are nearly identical to coastline values. Persistent directional winds below eight miles per hour appear to entrain and transport little ground dust. Variable winds or strong onshore winds greater than eight miles per hour entrain sufficient material over a five Km path to cause a two to threefold increase in total aerosol concentration. At these speeds, some salt spray is carried directly from the surf zone.

D. Replacement of Sea Salt Cl^- by NO_3^-

Marine aerosols reaching the southern California coast under persistent onshore wind conditions have an NO_3^-/Cl^- ratio that suggests that previous exposure to continental pollutants, most probably through coastal eddy circulations, has given the aerosol a "maritime" character.

In a marine environment where sea salt aerosol mixes with pollutants, the chloride in the aerosol can be replaced by nitrate in a one-to-one ratio with the degree of replacement depending on the relative humidity as well as the ambient concentrations of NO and NO_2. At relative humidities above the phase transition point (approximately 72 percent), there is a rapid change in the nitrate-chloride equilibrium, favoring the replacement of chloride by nitrate.

VIII. PUBLICATIONS

Two publications were prepared in part or totally as a result of studies done on this grant.

(1) Green, W. D., "Maritime and Mixed Maritime-Continental Aerosols Along the Coast of Southern California."

Delivered at

Working Symposium on Sea-Air Chemistry (WORKSSAC), Fort Lauderdale, Fla., January 31 - February 3, 1972.

Published in

Journal of Geophysical Research, Vol. 77, No. 27, September 20, 1972.

(2) Green, W. D., T. M. Mills, and Pamela S. McMurry, Interactions Between Marine and Continental Aerosol Sources.

Delivered at

International Symposium on the Chemistry of Sea-Air Particulate Exchange Processes, Nice, France, October 4-10, 1973.

To be Submitted for Publication in

Journal de Recherches Atmosphérigues.

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APPENDIX A

MARITIME AND MIXED MARITIME-CONTINENTAL AEROSOLS ALONG THE COAST OF SOUTHERN CALIFORNIA

A Paper by

William D. Green

Maritime and Mixed Maritime-Continental Aerosols along the Coast of Southern California

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Interactions between marine aerosols and polluted continental air were studied at a coastal sampling station in the Los Angeles basin. Material was collected on filters and salt-sensitive impaction slides over a vertical distance of 30 meters in order to contrast differences between fresh aerosols generated in the surf and aged aerosols entering the basin from the open ocean. The diurnal onshore-offshore flow of air was monitored to characterize short-term interactions between heavily polluted air and the marine environment. In the absence of well-defined scavenging mechanisms, the removal of nonmarine aerosols and the addition of sea salt during the 12- to 16-hour residence time over the ocean at night was minimal. Analysis of cascade impactor samples collected in relatively clear air indicated a deficiency of chloride in the smaller marine aerosols due to the inclusion of nonchloride particulates from continental sources or other mechanisms. The formation of a highly conductive acid species in these aged aerosols was noted. Large-scale mixing of nitrogen dioxide from continental air is postulated with reactions between salt particles and the gas leading to the formation of nitric acid and the loss of hydrogen chloride in the gas phase. The use of the term 'maritime aerosol' is suggested for mixtures of marine and continental aerosols in the coastal zone.

The coastal region near Los Angeles provides an excellent area to study interactions between marine aerosols and pollutants. During most seasons of the year, air flow across the coastline is characterized by a strong midday onshore flow followed by a weak offshore flow at night. The daytime onshore flow of maritime air is subjected to turbulent mixing over the land and contamination by pollutants. At night, the polluted air drifting offshore is altered by some additional mixing and the injection of aerosols directly from the ocean surface.

This paper discusses some of the observed variations in the chemical and physical properties of the maritime and mixed maritime-pollution aerosol as a function of residence time, addition-removal rates, and exposure to gaseous pollutants. Specific attention is directed to the mechanism whereby nitrogen dioxide can react with particles containing sodium chloride in the presence of water vapor to yield acid nitrates and hydrochloric acid.

Previous observations of the NO_3^-/Cl^- ratio in giant sea-salt particles from coastal marine air near urban areas indicated the possible reaction between sea salt and NO_x [*Junge*, 1956]. In some cases, the NO_3^-/Cl^- ratio in the coastal zone was ten times larger than that found in purely continental or clean marine air.

Robbins et al. [1959] postulated that NO_2 is hydrolyzed in the vapor phase to HNO_3 according to the reaction:

$$3\ NO_2 + H_2O_g = 2\ HNO_3 + NO \qquad (1)$$

Equilibrium for this reaction lies far to the right; however, at room temperatures and relatively high humidities, about 5% of the NO_2 is converted to nitric acid. Since salt particles are hygroscopic and dissolve in their own condensed moisture at relative humidities above 75%, the direct reaction:

$$2\ NO_2 + H_2O_l = HNO_2 + HNO_3 \qquad (2)$$

is also a source of nitric acid.

Experimental laboratory evidence indicated that these reactions, as well as the reaction

$$HNO_3 + NaCl = NaNO_3 + HCl \qquad (3)$$

were feasible atmospheric mechanisms. The re-

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action in (3) was relatively fast, the equilibrium constant ranging between 2 and 6. With mole ratios between 10 and 20 for NO_2/NaCl (equations 1 or 2 plus 3), 10% to 80% of the NaCl was converted to $NaNO_3$, depending on the relative humidity.

We will not attempt to define these reactions specifically for the Los Angeles area; however, the data presented do support the conversion of salt particles to acid aerosols with a systematic change in the Cl^-/Na^+ ratio due to a loss of chlorine.

LOCATION AND METHODS

A building, located about 100 meters from the shoreline at El Segundo, California, provided a unique opportunity to sample vertical profiles of the maritime aerosol near the coast. Two elevations were used: one at the 8-meter level to sample background aerosol mixed with a large surf spray component, and another at the 30-meter level to obtain material more representative of the maritime aerosol. In the following discussions, the term 'maritime aerosol,' or the mixture of marine and continental aerosols produced along the continental boundary, is used in contrast to the pure 'marine aerosol' that is generated exclusively over the open ocean.

Aerosol samples for mass loading and chloride analysis were collected on type A glass fiber filters with a low chloride blank (0.005 mg/filter). Specially coated glass slides with chloride-sensitive films [*Cadle et al.*, 1950; *Lodge*, 1954; *Green*, 1968] were used in a Unico cascade impactor to determine the distribution of salt particles as a function of size. Additional samples were collected on porcelain fallout plates exposed for periods of 2 to 4 weeks to determine long-term chemical changes.

Wind speed, direction, and relative humidity were monitored continuously during and before each sampling trip. The meteorological data were used to estimate the wind trajectories and prior history of the air masses, particularly in cases where continental or polluted air was mixed over the ocean.

Filters were weighed, and soluble salts washed from the filters were analyzed for chloride, specific conductivity, and acidity. Wash water from the fallout plates was analyzed for sodium, as well as for the above components.

The chloride analyses were used to calculate sea-salt equivalents in the total aerosol samples. This procedure initially assumed that the ocean was the only source of soluble chloride particles and that the Cl^-/Na^+ ratio was the same as the sea-water value of 1.797. Observed dilutions of the marine aerosol with particles not containing chloride, as well as strong evidence of changes in the Cl^-/Na^+ ratio due to reactions with pollutants, invalidated this equivalency calculation. Sea-salt equivalents as presented in the next section were calculated from the residual chloride values. Deviations of the aerosol composition from pure sea salt reflect a combination of dilution and reaction without preference for either mechanism.

RESULTS

Several distinct variation patterns were noticed in the equivalent sea-salt content of the aerosol as a function of time of day, source of the air, and distance above sea level. In many cases, the material sampled at the lower level near the shoreline was quite different from the material collected 30 meters above sea level.

Variations with Time of Day

Surface meteorology in the Los Angeles basin is characterized by a diurnal onshore-offshore flow of air. As the relatively polluted air moves offshore at night, a small salt-rich aerosol component is injected from the surf line.

In the summer and fall, the offshore flow generally reverses about 0700–0900 in the morning. In the winter, this reversal may be delayed until about 1100–1300 or may be absent completely. Once the reversal occurs, a mass of polluted air that had been exposed to the marine environment for progressively longer periods of time during the previous evening is moved onshore. Samples collected throughout the day can be used to study interactions between marine aerosols and pollution components as a function of time.

In Figure 1, the percentage equivalent sea salt in the total sample as calculated from the chloride analysis is plotted against the time of day the sample was collected. The pattern seen in Figure 1 was observed on many days throughout the year and is presented here for illustration only. As was noted earlier, the apparent deficiency in sea salt reflects the degradation of

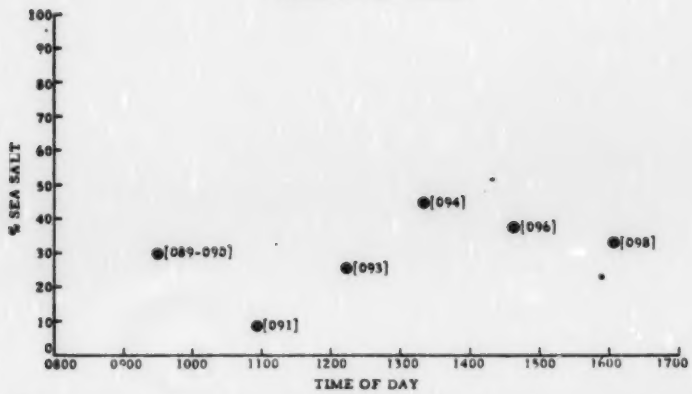

Fig. 1. Per cent sea salt in aerosols taken from high-volume filter samples 30 meters above sea level at El Segundo, California, September 2, 1971. Values in braces are filter numbers.

chloride in concentration by dilution or reaction to the gaseous phase.

On this date (September 2, 1971), the onshore flow started about 0830. The first sample collected at about 0930 appeared to contain considerable surf salt. By 1100, the air had lost its major salt loading owing to vertical mixing or fallout of large particles.

At about noon, the seaward 'smog front,' marked by a sharp increase in the salt content, passed the sampling station. Before that time, the sampled air consisted of mixed marine and polluted air that had moved offshore the preceding evening. The low salt content of the late morning samples on this and other dates implies that salt is added very slowly, an observation that is compatible, in a converse sense, with estimated residence times of 3–12 days for typical marine aerosols. Similarly, little evidence exists for the rapid removal of pollution aerosols over a period of 12–16 hours.

The decrease in the percentage of salt later in the day was observed on nearly all sampling days during the summer and fall. One possible explanation, based on the loss of chloride through reactions with NO_x, will be discussed later.

Because of the delayed initiation of onshore flow in the winter, a similar decrease was not observed late in the day. With this exception, the composition of the aerosol was similar, as can be seen in Figure 2, which is a composite of samples taken between December 22, 1970, and January 7, 1971, at the same level, 100 feet above the surf line.

Figure 2 is an alternate presentation of the data, where salt values are computed in terms of flux rather than concentration or percentage as in Figure 1. Distance of the air source from the shoreline was determined from the total wind run before and during sampling.

Salt Particle Distributions

Chloride-sensitive films were used in a Unico cascade impactor to determine the relative numbers of chloride-containing particles in the total aerosol sampled as a function of size, distance above the surf line, and time of day.

In Table 1, the number ratio of chloride particles collected at the 8-meter level to the number at the 30-meter level was computed for various size categories on the two representative dates. Because of the time required to reduce this type of data, additional sets of data were not available.

As was expected, nearly all the surf-spray-enriched samples taken at the 8-meter level contained more salt per unit volume. Two peaks in the size distribution of the surf component are indicated at about 12 μ and around 22–26 μ. The only exception occurred in the largest sizes on the morning of January 7, 1971, probably because of previous vertical mixing of spray particles to the 30-meter level.

In Table 2, the percentages by number of chloride-containing particles sampled on each of the four cascade impactor stages are reported. The samples collected on six different days in December and January were grouped into three

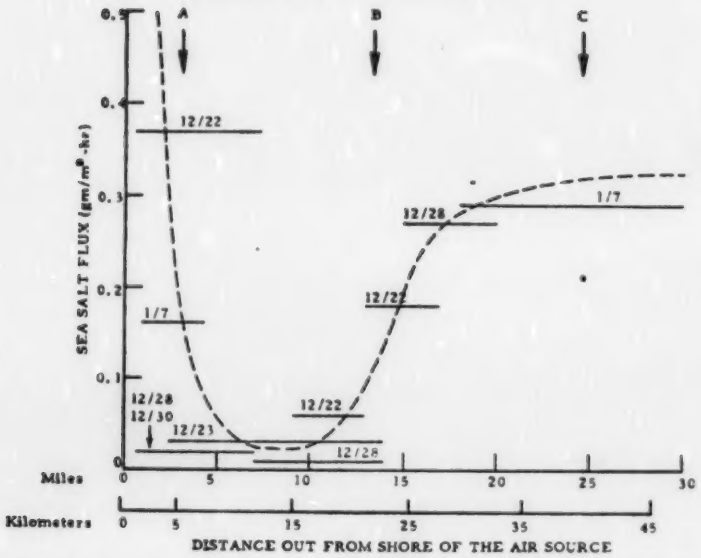

Fig. 2. Sea-salt flux versus air source. A, approximate point where most surf particles 10 μm in diameter or larger have fallen out; B, seaward smog front; C, increasing contribution of salt from open ocean.

major categories or composites based on previous meteorological history.

Composite 1 consists of samples collected in polluted air that had moved out over the ocean earlier in the evening. At the initiation of the next onshore breeze, this air was 8–20 km offshore (Figure 2) and had lost the principal surf component by mixing and precipitation.

Composite 2 represents near-shore air (0–8 km offshore) where the surf component added during outward transit is still evident.

Composite 3 is maritime air from a distance greater than 20 km offshore. This air contains no immediate pollution component from the diurnal offshore flow; however, the possibility of larger-scale mixing of continental contaminants into this air is indicated by the presence of nonchloride particles on stage *D*.

In all cases, the largest particles (>5.5–7.0 μ) were nearly all sea salt. At the lower level (8 meters), the addition of surf spray in all size ranges is evident as the air passed inland.

Chemical Properties

It was assumed in the past that aerosols formed over the ocean were the simple residue of evaporated sea salts. Today, many mechanisms, including ion fractionation and the stripping of organic films from the ocean surface, have been identified as possible sources of aerosols that deviate from the sea-salt composition [*Stumm and Imboden*, 1972, and other papers in this issue]. Local contamination of the air in the coastal region is an additional mechanism leading to compositional deviations.

A total of twelve sampling trips were taken during the period of investigation from December 1970 through September 1971. In all cases,

TABLE 1. Relative Number of Chloride-Containing Particles at 8 and 30 Meters above Sea Level

Diam., μ	December 28, 1970		January 7, 1971	
	Morning	Afternoon	Morning	Afternoon
3	1 6	1 3	2 6	1 4
6	2 0	2 4	2 4	1 9
9	2 2	6 2	2 4	2 4
12	2 6	6 7	3 5	4 2
15	1 5	5 1	1 1	2 2
18	4 4	3 6	0 8	1 6
22	6 0	5 0	0 6	1 4
26	4 0	5 2	0 5	3 2
30	1 5	3 0	<0 9	3 0

Ratio of the number per cubic meter at 8-meter level to the number per cubic meter at the 30-meter level.

TABLE 2. Percentage by Number of Chloride-Containing Particles in Various Types of Maritime and Near Coastal Air

Stage	MMD, μ	Composite 1 (Pollution)		Composite 2 (Pollution with Surf Component)		Composite 3 (Maritime)	
		30-Meter	8-Meter	30-Meter	8-Meter	30-Meter	8-Meter
A	>5.5–7.0	97	93	93	97	90	99
B	5.5–7.0	78	94	90	93	78	80
C	2.8–3.5	48	90	65	78	74	85
D	1.5–2.0	7	38	25	58	28	48
Total per cent chloride particles by number		33.6	65.2	49.8	70.5	52.8	67.5
Enrichment ratio, % 8 m/% 30 m		1.94		1.41		1.28	

the samples collected were deficient in chloride ion relative to the expected chloride to total dissolved solids ratio in sea water.

In Table 3, the percentages by weight of equivalent sea salt, as derived from the chloride ion analysis, are listed for the 8-meter and 30-meter levels at El Segundo. In addition, an enrichment ratio between the two levels was calculated as in the case of the data in Table 1. These chemical data support the single-particle chemical assessments made in Tables 1 and 2. Nearly all samples collected at the lower level were enriched in salt from the surf zone, while at the same time none of the aerosol samples approached a pure marine composition.

One particularly notable fact is the chloride deficiency in the relatively uncontaminated aerosol sampled late in the day, after the inward passage of the polluted air. Equivalent sea salt, as calculated from the chloride ion, was lowest late in the afternoon.

Two probable causes of these anomalies can be postulated.

1. *Production of non-chloride-containing particles over the ocean.* Some ion fractionation could occur, resulting in a decrease in the chloride-to-sodium ratio; however, current evidence, from mid-oceanic samples, does not support this mechanism. An alternate mechanism would be the aerosolization of organic materials during bubble film bursting

TABLE 3. Percentage by Weight of Equivalent Sea Salt in Aerosol Samples Calculated from the Chloride Ion Concentration

Time	8-Meter Level, Mixed Surf and Maritime Aerosol	30-Meter Level, Maritime Aerosol	Enrichment Ratio, % 8 m/% 30 m
	September 2, 1971		
1050	15	9	1.7
1215	46	25	1.8
1320	53	41	1.3
1440	50	38	1.3
1605	47	32	1.5
	September 30, 1971		
1010	44	21	2.1
1150	44	22	2.0
1330	67	45	1.5
1455	68	68	1.0
1620	43	32	1.3

with an associated negative shift in the mass of chloride in the small size spectrum. Since these films are surface active and generally hydrophobic, the over-all composition of the soluble salt fraction should not be altered. No change in the Cl^-/Na^+ ratio or acidity of the material should occur.

2. *Large-scale mixing with continental air.* Complex eddy circulation patterns along the coast of California can result in the transport of continental air over the ocean. At sea, this air is mixed and appears at a later time with the return circulation. The net result is the injection of continentally derived gases such as ozone, oxides of nitrogen, and sulphur dioxide into the marine layer, and the general mixing of particulates not containing chloride with the lower end of the marine size spectrum. The residence time and available scavenging mechanisms would control the probability that these particles and gases can survive to reappear along the shoreline. Reactions involving the mixed gases and salt particles could result in the oxidation of chloride ion, loss of gaseous chlorine, and an associated development of acid in the aerosol particles.

In order to test the second postulate, the samples collected on September 2 and 30 were analyzed to determine the specific conductivity and pH as indicators of acid formation. The two dates selected for comparison (September 2 and 30, 1971) were similar in meteorology. The onshore breeze initiated about 0830, and the smog front passed inland about noon. The principal difference was a higher level of pollution and nonmarine particulates on September 2.

Certain complications arose in the direct measurement of pH owing to the basic nature of the filters; however, results indicated that the maritime aerosol collected at the 30-meter level was more acidic than the surf-spray-enriched aerosol at the lower level. Slight, but inconclusive, changes were noted with time of day.

The conductivity measurements in Table 4

TABLE 4. Conductivity of Maritime and Surf-Enriched Maritime Aerosols

Filter No.	Sampling Period	% Equivalent Sea Salt	Conductivity, μmho/cm: Per mg Total Aerosol	Conductivity, μmho/cm: Per mg Cl^-
September 2, 1971; 30 Meters above Sea Level, Maritime				
089–090	0855–1055	29	84.2	902
091	1011–1136	9	48.1	1010
093	1145–1245	25	76.7	613
094	1251–1351	41	93.3	494
096	1411–1511	38	92.0	511
098	1519–1655	32	102.0	680
September 2, 1971; 8 Meters above Sea Level, Surf-Enriched Maritime				
092	1011–1136	41	41.0	508
095	1257–1357	53	67.3	240
097	1531–1645	47	60.4	234
September 30, 1971; 30 Meters above Sea Level, Maritime				
179	0930–1100	21	61.8	537
177	1104–1234	22	52.3	438
175	1237–1407	45	138.0	607
173	1410–1541	68	157.0	497
171	1545–1700	32	91.0	541
September 30, 1971; 8 Meters above Sea Level, Surf-Enriched Maritime				
178	0940–1110	44	52.6	219
176	1112–1242	44	42.7	179
174	1244–1424	67	58.9	161
172	1426–1556	68	68.1	186
170	1558–1710	43	48.5	197

support the inferences based on the *p*H analysis. Maritime aerosols collected well above the surf zone on both days were more conductive on a per milligram basis than the same aerosols after enrichment with surf spray. Relative conductivity increased at the upper level later in the afternoon after the passage of the diurnal pollution. Over-all conductivity per milligram of aerosol varied directly with the percentage of equivalent sea salt; however, the conductivity per unit mass of chloride ion displayed a general inverse relationship. The highest values were recorded early on September 2, when the air was most polluted. These observations support the hypothesis that the maritime air above the surf zone in southern California contains an acidic, relatively conductive aerosol component that is present in concentrations inversely proportional to the chloride ion concentration.

Further evidence for the production of this acid species at the expense of chloride ion was derived from the analysis of samples washed from fallout collectors during August and September 1971. These surfaces were mounted before the aerosol sampling program and were washed periodically with distilled water at two- to four-week intervals. All samples were analyzed for sodium, chloride, and *p*H. The results are plotted in Figure 3.

Sodium varied slightly in the samples; however, the ratio of sodium to total soluble solids never exceeded the sea-water value. Some contamination occurred from nonmarine sources, but the nature of this contamination did not cause the observed decrease in the Cl^-/Na^+ ratio. The principal change was due to the loss of chloride ion and an associated increase in acidity. Selected analysis of these samples revealed the presence of nitrate ion.

Discussion

In the foregoing discussion, a distinction was made between two major types of aerosol populations in the air along the coast of southern California. The first type was a predominately pollution aerosol with a small marine component added during the diurnal offshore flow pattern. The second is a maritime aerosol derived essentially from the open ocean; however, the results indicate that this type is also polluted by larger-scale air circulation along the coast. When air is sampled close to the ground near the coast, a second subcategory must be added

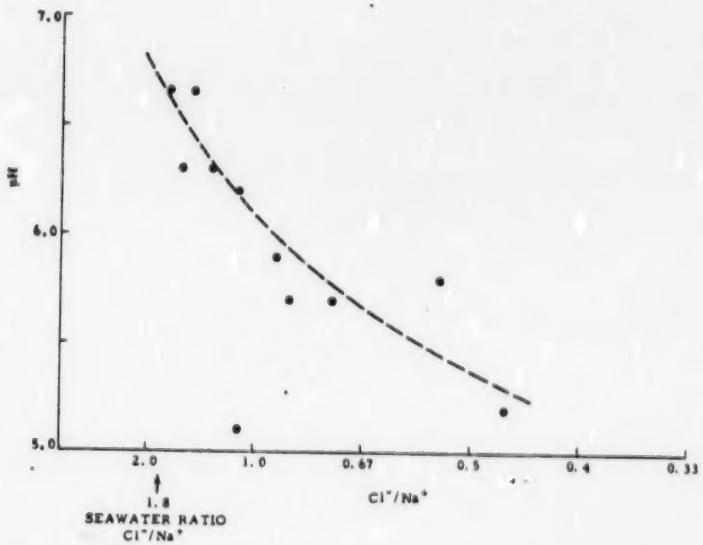

Fig. 3. Variation of *p*H with Cl^-/Na^+ ratio (*p*H of sea water is about 8.0) in samples from fallout collection surfaces in the southern California coastal zone.

to the two principal types to account for the aerosol component derived directly from the surf.

The percentage of sea-salt particles in the pollution aerosol, as calculated from the chloride ion concentration, is low owing to the dilution of the total population by small particles in the range <1.0–$2.0\ \mu$ (Table 2). Salt derived from the surf zone can enrich the salt particle population momentarily in air near the ground.

Maritime aerosols collected from air that originated from areas outside the diurnal coastal zone were also deficient in apparent salt content. Similar observations have been made in the past along the California coast [*Holzworth*, 1959]. Chloride analysis of samples taken at Southeast Farallon Island in 1956 yielded sea-salt equivalents of only 70% for oceanic aerosols. These values dropped to 48% for air with an identifiable coastal component and were as low as 10% for air exiting directly from the San Francisco Bay area. Similar deficiencies were noted at Cresent City, Point Piedras Blancas, and San Nicolas Island.

Chemical analysis of maritime samples during the present study implies the presence of an acidic component in the aerosol that is more conductive than sea salt. The concentration of this component is directly proportional to the deviation of the chloride ion concentration from the expected sea-salt composition. The existence of a nonchloride acid can be inferred if the reactions presented by *Junge* [1956] and *Robbins et al.* [1959] are applicable to the southern California coastal region. In that case, nitrogen dioxide, carried seaward in the eddy circulation, would react upon mixing with salt particles to form HNO_3, HCl, and possibly Cl_2. Chlorine gas would be lost, along with some of the hydrogen chloride, to yield an aerosol enriched in acid nitrates.

Further analytical work is required to verify the specific nature and degree of these reactions. Short-term diurnal mixing of polluted air over the near coastal regions does lead to acidification of the aerosol; however, the over-all conductivity and acidity do not approach the values observed in the maritime aerosol. The maritime aerosol appears to contain an acid species that results from the long-term interaction between small salt particles and large-scale intermixing with continental air.

CONCLUSIONS

1. *Redefinition of marine aerosols.* Results of the current study indicate the need to redefine the concept of a marine aerosol. In southern California and many other areas of the world, the offshore mixing of continental and marine air leads to the formation of a hybrid aerosol mix that is only quasi-marine in nature.

It is proposed that the term 'marine aerosol' be reserved for those particulates that are sampled in mid-oceanic regions under highly controlled conditions. Some independent criteria should be used, such as the Aitken-condensation nuclei count, to define the purity of the air before sampling. Each presentation of data should include this or other suitable criteria.

The term 'maritime aerosol' is used here to define those aerosols in the marine environment that result from the mixing of marine and continental air masses.

2. *Classification of air types.* Along the coast of southern California, it is possible to define two principal types of aerosols in the marine environment: (1) pollution-maritime and (2) maritime. Under special conditions of persistent onshore flow, a third type may be present that approaches the pure marine aerosol; however, no such aerosol was encountered during the present study.

The maritime aerosol, consisting of a mixture of continental and aged marine aerosols, was sampled late in the day after localized sources of polluted air were removed by the onshore sea breeze. The pollution-maritime type occurred after the reversal of the offshore flow.

3. *Size distribution.* The principal variation in the chemistry of the aerosol occurred in the lower size ranges. The percentage of salt particles below 1–2 μ varied by 2 to 4 over a vertical distance of 22 meters. Very little variance in the giant particle composition was noted with altitude or type of air being sampled. More than 90% of the particles sampled at an MMD greater than 5.5 to 7.0 μ contained salt.

4. *Conductive-acidic aerosols.* The most conductive and acidic aerosols were sampled 30 meters above the ground in the mid- to late afternoon. The presence of a surf component in the same air at the lower level reduced both the conductivity and the acid content of the aerosol. Chemical analysis supported the hypothesis that

nitrogen dioxide from continental sources was mixed with salt aerosols in the marine layer, leading to reactions between the gas and chloride ion. The loss of chloride as HCl or Cl_2 with an associated decrease in the Cl^-/Na^+ ratio and an increase in acidity due to the formation of nitric acid is implied.

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APPENDIX B

INTERACTIONS BETWEEN MARINE AND CONTINENTAL AEROSOL SOURCES

A Paper by

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INTERACTIONS BETWEEN MARINE AND CONTINENTAL AEROSOL SOURCES

ABSTRACT

Variations in the physical composition and chemical character of marine aerosols as a result of interactions with continental aerosols and gaseous pollutants have been studied for several years along the coast of Southern California. Localized mixing of urban air over the ocean and inland transport of both highly contaminated maritime air and relatively clean oceanic air were studied to determine short and long range changes in the marine aerosol. In some cases, mixed maritime and continental aerosols were traced meteorologically to sources in the Pacific Northwest.

The occurrence of nitrates in the marine aerosol and associated deficiencies in chloride supports evidence for reaction mechanisms between salt particles and oxides of nitrogen. Data on the aerosol size distribution, chemical composition and meteorological source of air masses sampled over a three-year period have yielded very few cases where uncontaminated or unaltered marine aerosol was observed.